

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/238525634>

Kedge Absorption spectra in Warm Dense Matter

Article · September 2009

DOI: 10.1063/1.3241191

CITATIONS

2

READS

128

11 authors, including:



Olivier Peyrusse

Aix-Marseille Université

192 PUBLICATIONS 3,329 CITATIONS

SEE PROFILE



Stephane Mazevet

Observatoire de la Côte d'Azur

154 PUBLICATIONS 5,883 CITATIONS

SEE PROFILE



Marion Harmand

Sorbonne Université

89 PUBLICATIONS 1,894 CITATIONS

SEE PROFILE



Anna Levy

Sorbonne Université

63 PUBLICATIONS 2,027 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:



APOLLON [View project](#)



Intense laser irradiation [View project](#)

K-edge Absorption spectra in Warm Dense Matter

O. Peyrusse*, S. Mazevet[†], V. Recoules[†], F. Dorchies*, M. Harmand*, A. Levy*, J. Fuchs**, A. Mancic**, M. Nakatsutsumi**, P. Renaudin[†] and P. Audebert**

*CELIA, UMR 5107, Université Bordeaux I - CEA - CNRS, 351 Cours de la Libération, Talence, FRANCE

[†]CEA, DAM, DIF, F-91297, Arpajon, FRANCE

**LULI, UMR 7605, Ecole Polytechnique, 91128 Palaiseau, FRANCE

Abstract. The recent development of compact, short (ps or sub-ps) X-ray sources gives access to the structural nature of short time-scale phenomena and to the study of very transient systems such as warm dense materials. Among the structural tools used for the study of static (solid) materials, X-ray Absorption Fine Structure (XAFS) spectroscopy has proven to provide useful information on the local structure (atomic arrangement) and on the electronic Density of States. In a context where the matter is disordered but highly correlated, we present K-edge absorption studies of warm, dense aluminum. The range of temperature starts from the solid and extend to the strongly correlated plasma regime. We describe here two theoretical approaches for the calculation of the K-edge absorption features. The first one involves a (Modified) HyperNetted Chain - Neutral Pseudo Atom (MHNC-NPA) model of dense matter coupled with a specific model of the XAFS features. The second one is based on *ab initio* Quantum Molecular Dynamics (QMD) simulations from which a Kubo-Greenwood formulation combined with the Projector Augmented Wave (PAW) formalism gives a direct access to the X-ray absorption spectra. These spectra are compared with recent K-edge absorption measurements in aluminum targets isochorically heated by laser-created protons and probed by a short X-ray backlighting source.

Keywords: Warm Dense Matter, XAFS

PACS: 78.70.Dm, 61.10.Ht, 52.27.Gr

INTRODUCTION

The emerging new field of ultrafast absorption spectroscopy [1] is seeded by the development of short (picosecond or subpicosecond) X-ray sources. In that context, one can study transient states of matter such as the so-called warm dense regime, i.e. a regime embracing the solid-, the liquid- and the plasma-state. A slightly reduced domain of the WDM is the isochorically heated matter regime where the density remains close to the solid density while the temperature varies between the ambient temperature and a few eV. The study of this state of matter is particularly challenging both from an experimental point of view and from a theoretical point of view. On the experimental side, these studies make use of pump-probe techniques, time-resolved apparatus and require the developement of short and bright X-ray sources [2]. On the theoretical side, various approaches for the description of the electronic structure of matter in the conditions mentioned above are available [3]. They make use of different numerical techniques and the calculation or the simulation of specific observable quantities may require the devel-

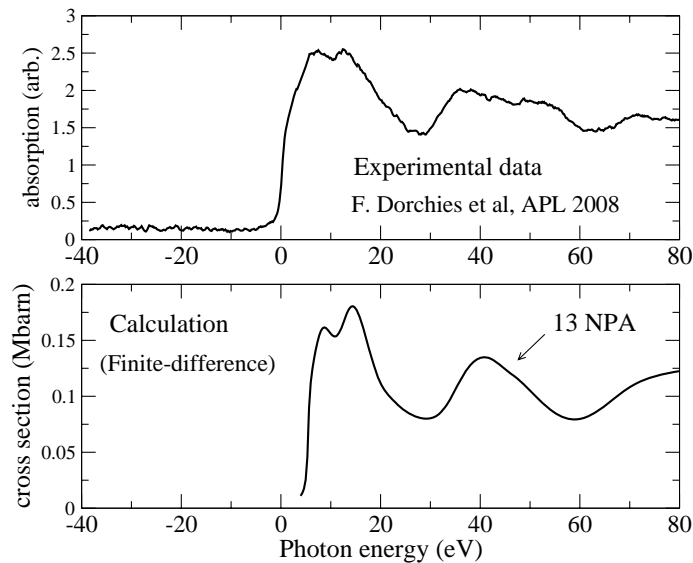


FIGURE 1. K-edge XAFS spectrum of cold (fcc) aluminum - Top: experimental spectrum, bottom: Finite Difference calculation for a cluster of 13 NPAs (a central atom + the first coordination shell).

opement of new numerical tools. Among the observable quantities, the spectral profile of a photoabsorption edge is particularly interesting because of its known sensitivity to the local atomic arrangement. This spectroscopy also known as XAFS (for X-ray Absorption Fine Structure) spectroscopy has a long history which starts from the use of synchrotron radiation as a probe for the study of solids and molecules. It is related to the interpretation of the modulations observed above a photoabsorption edge. The energy range of these modulations is usually separated into two regions. The region that remains close to edge (< 50 eV) is the so-called XANES (X-ray Absorption Near Edge Spectroscopy) region. Beyond this somewhat arbitrary defined region, one speaks rather of EXAFS (for Extended X-ray Absorption Fine Structure) spectroscopy. The work here describes two theoretical approaches used for the calculation of both the properties of Warm Dense Matter and its specific application to K-edge profiles in this regime. Results are compared with experimental measurements on isochorically heated samples of aluminum.

PHOTOELECTRIC EFFECT IN DENSE MATTER

As mentioned above, XAFS spectroscopy consists of studying the modulations of the absorbed radiation beyond the photoionization thresholds. A clear example of this phenomenon is shown in Fig. 1(a) which displays the profile of an aluminum K-edge. This spectrum has been obtained with a table-top X-ray source but similar spectra have already been obtained with synchrotron radiation [4].

To explain these structures, the starting point is the expression of the photoelectric cross section

$$\sigma(E) = 4\pi\alpha\hbar\omega \frac{2m}{\hbar^2} \sum_L |\langle \psi_{Lk} | \vec{\epsilon} \cdot \vec{r} | \phi_i \rangle|^2 \quad (1)$$

This expression is just a form of the Fermi Golden rule. $\vec{\epsilon}$ is the x-ray polarization vector, $|\phi_i\rangle$ is a core state (1s for K-edge) and $|\psi_{Lk}\rangle$ [where $L \equiv (\ell, m)$] is a continuum state. Furthermore, we note that $E = k^2/2$ and the calculation starts from the fermi level at zero-temperature. For non-zero temperatures, a vacancy factor $1 - f(\mu/kT)$ (where f is the Fermi occupation factor, and μ is the chemical potential) must be added on the right side of Eq. (1). In dense matter, the photoelectron wavefunction $|\psi_{Lk}\rangle$ is a *multiatom* wavefunction in the sense that it depends on the position of the neighboring atoms (with respect to the photoionized atom) which are responsible for the modulations observed in Fig. 1. For a given state (ρ, T) of the material, the spatial position of these atoms relies on a specific model of dense matter.

THE MODELING OF WARM DENSE MATTER

We briefly discuss here two approaches to the warm dense regime of matter. The first one is a liquid-metal approach. It gives only spherical averaged quantities, e.g. the radial distribution function $g(r)$. For generating XAFS spectra, such an approach involves necessarily a *sampling* of the calculated $g(r)$. By sampling, we mean the random determination of atomic configurations whose interatomic spacings are representative of a given correlation function, $g(r)$. Once this set of configurations is determined, a specific calculation of the wavefunctions $|\psi_{Lk}\rangle$ can be done from which the photoionization cross section is obtained. The second method discussed here is the traditional solid state approach based on electronic structure calculations on ionic configurations obtained using Quantum Molecular Dynamics (QMD) simulations. In the latter, the electrons are treated quantum mechanically while the ions are propagated in time classically to obtain the structure of the medium at a given density and temperature. The integrated nature of the simulations provides a consistent set of properties ranging from dynamical (EOS), electrical, optical and, more recently, X-ray properties [6].

(M)HNC - NPA

This approach is based on the Neutral Pseudoatom (NPA) concept first introduced by Ziman in solid-state physics [7] and later used in the context of dense plasma physics [8]. A NPA is made of a core of bound electrons and a cloud of valence electrons so that the electron density around a pseudoatom is written as $\rho_{el}^{(NPA)}(r) = \rho_c(r) + \Delta n(r)$. The cloud $\Delta n(r)$ is due to the electrons of the electron gas (in which an ion core is immersed) that tend to distribute so as to form a screening cloud about the ion core. Each NPA is then taken as a primary building block. They can interact with each other through an effective pair potential ϕ_{eff} . (Modified) HyperNetted Chain (HNC) equations then give the $g(r)$ function. The term "Modified" comes from the addition of a so-called *Brigde*

function [9, 10] into the HNC equations. The pair interaction ϕ_{eff} depends on Δn and on an effective pseudopotential deduced from Δn at the linear response approximation [8]. $\Delta n(r)$ is independently obtained from the model of an *atom in a jellium vacancy* [11] extended to finite-temperatures. Here, a simple Local Density Approximation (LDA) formulation of the exchange potential has been used. Various comparisons of the $g(r)$ functions obtained with this kind of model with direct simulations have shown that this approach is fairly sound in the liquid-state regime as well as the plasma regime.

QMD simulations

In QMD, the system evolves temporally according to a two-step procedure. First, a representative cell of atoms is defined. This cell is replicated throughout space. For a fixed configuration of the ion cores, one performs a quantum-mechanical calculation of the electronic state. From this electron state, a force acting on each ion core is determined. The ion cores are then advanced by the classical equations of motion. Here, we used the ABINIT code [12] with a Projector Augmented Wave (PAW) [13] generated pseudopotential in the Generalized Gradient Approximation (GGA) parametrization of density functional theory. Pseudowavefunctions for the valence electrons are then the primary objects in these calculations. For the conditions of isochorically heated aluminum with $T \leq 10$ eV, the PAW pseudopotential was constructed with three outer electrons ($3s^23p$) and the simulations were performed at the Γ point and with a plane-wave cutoff of 15 Hartree.

XANES DATA

From the (M)HNC Model. Unlike the QMD model, the (M)HNC model gives only mean quantities like the $g(r)$ function. So, one must resort to a procedure for determining the atomic positions in a given cluster. In other words, one has to find the configurations that ‘sample’ the $g(r)$ function. We obtained these configurations from a least square method [14]. Unlike Ref. [14] where the subsequent calculation of the photoelectron wavefunction was based on the Multiple-Scattering (MS) theory, we used a finite-difference method (FDM) which allows one to remove the Muffin-Tin approximation of the interstitial potential which is inherent to the MS approach. If the Muffin-Tin approximation has proven to be very efficient in dense solid materials, it is less guaranteed in disordered matter. Although computer-time intensive, the FDM is another way to solve the Schrödinger equation (for the photoelectron wavefunction) directly onto a 3D cartesian grid. Our approach is close to the one proposed by Joly [15]. The space is divided into three regions: (i) an outer sphere surrounding the cluster of interest where the potential is supposed to be constant, (ii) an atomic region composed of very small spheres (up to a radius of 0.8 \AA , i.e. much smaller than the Wigner-Seitz radius) where spherical solutions are used, and (iii) the interatomic region where the FDM formulation is performed. The embedding technique of the spherical solutions onto the 3D cartesian grid is the one proposed by Thijssen and Inglesfield [16]. In region (iii) the unknowns are the values of the wavefunction on each grid point. Having in hand

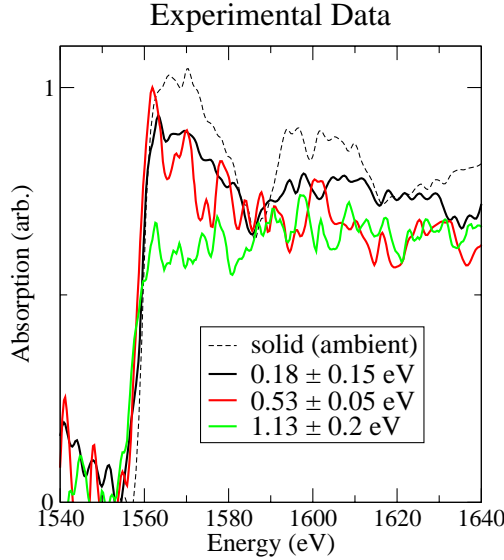


FIGURE 2. Experimental K-edge (XANES) spectra of an aluminum sample isochorically heated by protons.

the whole photoelectron wavefunction, the photoionization cross section [Eq. (1)] can be calculated. For the well known fcc geometry of solid aluminum, such a procedure is illustrated in Fig. 1(b), which displays a calculation performed for a cluster of 13 atoms only (a central atom and the first coordination shell). The total electron density was simply described by the superposition of the NPAs calculated at the solid density and at a temperature of 0.028 eV. In the disordered matter, such a calculation must be repeated for a significant number of spatial configurations and the cross section averaged.

From QMD. To obtain the optical response in the X-ray domain, one selects equally spaced ionic configurations along the equilibrated part of the trajectory. QMD calculations give a consistent set of properties by using the Kubo-Greenwood formulation (linear response theory) which gives the real part of the optical conductivity and from which the absorption coefficient can be obtained. Because of the use of a pseudopotential, the electrical and optical properties are, in principle, restricted to photon energies where only the outer electrons participate. However, within the PAW formalism, it is possible to construct matrix elements of the dipole operator connecting core and valence states and obtain the optical conductivity in the X-ray range [6].

RESULTS: ISOCHORIC HEATING OF AN ALUMINUM SAMPLE

An experiment has been performed at the 100 TW LULI facility using first, a 300-fs laser beam and second, a 2-ps laser beam. The complete experimental setup is described

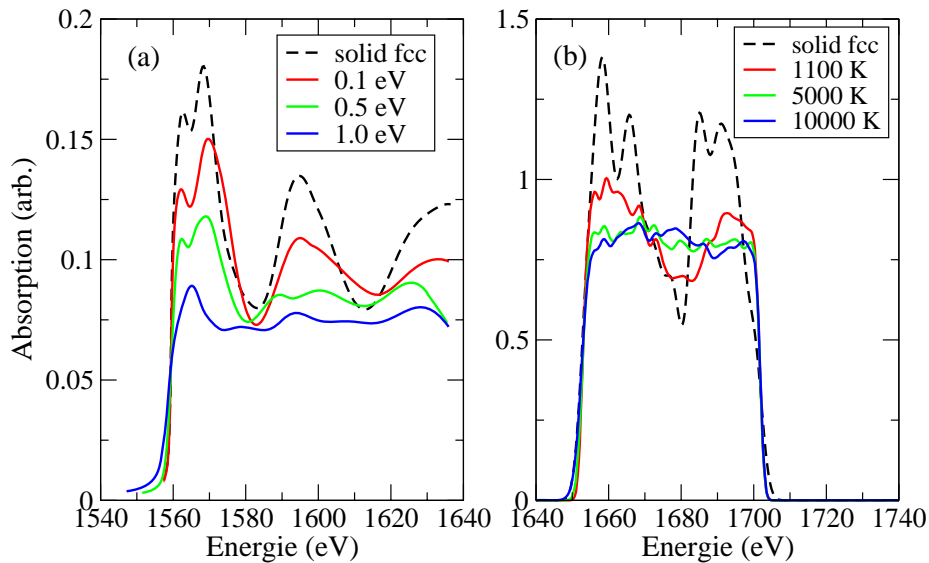


FIGURE 3. Calculated K-edge XANES spectra of aluminum as a function of the temperature (solid density), (a) (M)HNC-NPA model coupled with 3D FD calculations, (b) QMD data.

elsewhere [17]. In brief, the first laser beam was focused on a gold target, generating protons at the rear face. At some controlled distance, an aluminum sample was put in the proton path in order to be isochorically heated by the protons. In the mean time, or with some controlled delay, the second laser beam was focused on an erbium target giving a significant amount of X-ray photons in the spectral range of the Al K-edge. A simultaneous recording of the X-ray source and of the X-ray radiation transmitted through the sample allowed us to obtain temperature-dependant profiles of the K-edge (XANES) spectra. It is worth pointing out that the parameters of that experiment were mainly the energy of the protons created by the laser beam, the distance between the gold target and the aluminum sample, and the delay between this first and second beam creating the X-ray. Simulations and other diagnostics have shown that an isochoric and uniform heating of a sample can be obtained [17]. By varying the previous parameters, a set of temperature-dependant K-edge profiles has been obtained. Assuming a free electron gas behavior for the valence electrons, the corresponding temperatures have been obtained from the slope at the inflexion point of the edge. Results concerning the lower temperatures are plotted in Fig. 2. The cold spectrum is in good agreement with other measurements performed with other X-ray sources, which is rather satisfactory with regard to the "one-shot" character of the present measurements. Also, one clearly observe a loss of structure (in the spectrum) between a temperature of about 0.5 eV and of 1.1 eV. This change is obviously related to a structural modification in the heated material. Results of the calculations are given in Fig. 3. It is noteworthy that the experimental results and both of the calculations exhibit the same behavior, i.e. a loss of structure in a somewhat similar range of temperature. However, the (M)HNC-

NPA model (Fig. 3a) indicates this loss of spectral features for temperatures of about 1 eV. QMD data (Fig. 3b) indicate this loss of spectral structure for temperatures close to 0.5 eV.

CONCLUSION

X-ray Absorption Near Edge Spectroscopy which is a well known tool for the analysis of dense solid matter has been set in the context of Warm Dense Matter. It is clearly a valuable tool for studying states of matter between the solid, the liquid and the plasma. Experimental XANES spectra that have been obtained at these conditions are stringent tests for theoretical models. Presented results indicate the need to understand how the ionic structure influences the resulting XANES spectra.

REFERENCES

1. C. Bressler, and M. Chergui, *Chem. Rev.* **104**, 1781 (2004).
2. F. Dorchies, M. Harmand, D. Descamps, C. Fourment, S. Hulin, S. Petit, O. Peyrusse, and J.J. Santos, *Appl. Phys. Letters* **93**, 121113 (2008).
3. R.M. Martin, *Electronic Structure: Basic Theory and Practical Methods*, Cambridge University Press, Cambridge, 2005.
4. J. Wong *et al*, *Solid State Comm.* **92**, 559 (1994).
5. S. Mazevet, J. Kress, and L. A. Collins, “Quantum Molecular Dynamical Simulations of Warm Dense Matter,” in *Atomic Processes in Plasmas*, edited by J. S. Collins, S. Mazevet, and D. P. Kilcrease, AIP Conference Proceedings 730, American Institute of Physics, New York, 2004, pp. 651–654.
6. S. Mazevet, and G. Zérah, *Phys. Rev. Letters* **101**, 155001 (2008).
7. J.M. Ziman, *Adv. Phys.* **13**, 89 (1964).
8. F. Perrot, *Phys. Rev. A* **42**, 4871 (1990).
9. Y. Rosenfeld, and N.W. Ashcroft, *Phys. Rev. A* **20**, 1208 (1979).
10. F. Lado, S.M. Foiles, and N.W. Ashcroft, *Phys. Rev. A* **28**, 2374 (1983).
11. M. Manninen, P. Jena, R.M. Nieminen, and J.K. Lee, *Phys. Rev. B* **24**, 7057 (1981).
12. X. Gonze, *Comput. Mater. Sci.* **25**, 478 (2002).
13. P.E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
14. O. Peyrusse, *J. Phys.: Condens. Matter* **20**, 195211 (2008).
15. Y. Joly, *Phys. Rev. B* **63**, 125120 (2001).
16. J.M. Thijssen and J.E. Inglesfield, *Europhys. Lett.* **27**, 65 (1994).
17. A. Mancic *et al*, submitted to *High Energy Density Physics*, 2009