X-ray Absorption Near Edge Structures at the L_{3,2} and M_{3,2} edges: a Probe for the Electronic Behavior of Metal Nanostructures

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Abstract

We present a comparison of the calculation and experiment results of the X-ray Absorption Near Edge Structures (XANES) of the L_{3,2}-edges and the M_{3,2}-edges of representative 5d metals. Emphasis is placed on the first 10 – 15 eV above the Fermi level where the behavior of the relatively localized unoccupied d densities of states of transition metals across the periodic table can be probed. Experimentally, this is where the whiteline appears. The whiteline intensity contains information about the d holes at the metal site. We adopt a method of the Full Potential Linearized Augmented Plane Wave (FPLAPW) based on the Density Functional Theory with the modification of the exchange-correlation energy by Generalized Gradient Approximation (The Wien computer code). The calculation of electronic structure is performed starting by either compressing or expanding the lattices, to mimic nanostructural behavior. The results and their implications will be discussed.

Keywords: L-edge XANES, M-edge XANES, 5d metals, DFT, and GGA.

Introduction

The search for smaller and faster electronic devices is an impetus for nano-technology. Pursuing fabrication strategy of prospective nano-materials in general and striving for faster chips in computer industry in particular are some of the motivations behind the current endeavor of nano-material research. One of the objectives is to make nano size metallic contact that depends on the electronic properties of the materials. Down sizing of a metal cluster or crystal, yet maintaining its metallic integrity post an interesting challenge.

To delve into the quantum region of nano-matter is fundamental to understanding nano-devices. Semi-empirical potentials are inadequate to describe such quantum systems. Thus we use the first principle Local Density Approximation (LDA). Together with Generalize Gradient Approximation (GGA), self-consistent calculation renders realistic electronic properties of 5d metals as we present in this work.

DFT with GGA surpasses Hartree-Fock approximation [1] and X α calculation. DFT together with GGA provide a first principle understanding of the electronic and optical properties of 5d metals, including the behavior of their L_3 and M_3 XANES edges as shown from the following calculations. FPLAPW method is a better basis for metallic systems compared to muffin tin approximation or Gaussian orbitals, since it adds plane waves in interstitial area between atoms in crystals to describe delocalized conduction electrons.

Theory

DFT [2] shows that the ground state energy of an interacting in-homogeneous electron gas is given by the Kohn-Sham’s equation:

$$E = T[n] + \int v(r)n(r)d^3r + \int \left[ \frac{n(r)n(r')}{|r-r'|} - \frac{n(r')n(r)}{|r-r'|} \right]d^3rd^3r' + E_{xc}[n]$$ (1)

where T[n] is the kinetic energy functional of a system of N electrons, v(r) is the potential, n(r) is the density, and E_{xc}[n] is the exchange and correlation energy functional of an interacting system with density n(r).

The following coupled equations are to be solved self-consistently for N electron systems:

$$\left[ -\frac{1}{2} \nabla^2 + V(r) + \mu_{xc}(n(r)) \right] \psi_i(r) = E_i \psi_i(r)$$ (2)

$$\int \delta n(r) \left[ \frac{\delta T[n]}{\delta n(r)} + V(r) + \mu_{xc}(n(r)) \right] d^3r = 0$$ (3)

$$V(r) = v(r) + \int \frac{n(r')}{|r-r'|} d^3r'$$ (4)

Generalized Gradient Approximation [3] adds a gradient term $\varepsilon_{xc}^{GGA}$ (n,\nabla n) to the exchange-correlation energy functional to describe slowly varying density of electrons.
The exchange-correlation energy is given by the following:

\[ E_{xc}(r) = \int e_{xc}^{GGA}(r, \nabla n) d^3r + \int e_{xc}^{GGA}(n, \nabla n) d^3r + \ldots \]  

(5)

We have performed the self-consistent calculations numerically using the Wien computer code [4] for face center cubic (fcc) 5d metals, including Au, Pt, Ir, and Re. Full Potential Linearized Augmented Plane Wave (FPLAPW) method, where the basis at atomic sites are described by linear combinations of spherical harmonics and the interstitial region is occupied by plane waves, have been utilized. Scalar relativistic density functional was used with GGA modification. Self-consistent minimization of energy was achieved with 10000 k points to keep a high accuracy in each calculation. Tetrahedron method [5] for the k space integration was utilized.

**Experiments and Calculations**

1. **Bulk 5d Metals**

M3/2 and L3/2 edge XANES of transition metals have been obtained at the Canadian Synchrotron Radiation Facility at the Synchrotron Radiation Center, University of Wisconsin Madison and at the National Synchrotron Light Source, Brookhaven National Laboratory, respectively [6]. The data of 5d metals with fcc lattices are compared with the theoretical calculations based on DFT with GGA modification as shown in Fig. 1 and Fig. 2.

The theoretical and experimental L3 and M3 XANES show excellent agreement considering the DFT and GGA method is only an approximation and is generally good for interpreting close to ground state properties of matters.

The broadening of L3 and M3 edge is dictated by the natural line-widths of the 2p3/2 and 3p3/2 core holes and to a lesser extent, the instrument resolution. The natural line-widths of the 2p and 3p holes of 5d metals are typically around 6 to 7eV [7]. The calculated L3 and M3 edge spectra are convoluted with a 7eV Lorentzian broadening.

The 5d metals, Pt, Ir, and Re in decreasing occupancy of the 5d band, all possess a “whiteline”, an intense resonance at the onsets of both L3 and M3 edge XANES with increasing intensity whereas Au does not exhibit an intense whiteline. This can be explained by the location of their 5d band with respect to the Fermi level (Fig. 3) and the p-d dipole selection rule. The 5d band of Au lies entirely below the Fermi level and is nominally full while the other metal d bands spreads across the Fermi level and have localized unoccupied densities of d states just above the Fermi level.

**Fig. 1** Comparison of experiment and theory: M3 edges.

**Fig. 2** Comparison of experiment and theory: L3 –edges.
2. Nano-5d Metals

The Au and Pt nanostructures of interest were prepared on porous silicon substrates, with sponge-like silicon nanostructure prepared electrochemically [8]. Dendrite porous channels of the substrates provide nanogrowing beds for Au and Pt nano-crystallites. Typical L$_3$ edge XANES of Au and Pt nano-structures are shown in Fig. 4 and Fig.5, respectively. To mimic nano behavior, we incorporated the L-edge absorption of bulk Au and Pt with 5% volume contraction, respectively. It is interesting to note that the difference in the densities of states resulting from s-d re-hybridization is most noticeable at the whiteline.

Experimentally, these Au and Pt nano clusters exhibit face center cubic structure as revealed by their EXAFS (extended X-ray Absorption Fine Structures). The crystallite sizes are typically about a few nm. XRD (X-ray powder diffraction) of Au shows a slight contraction, about a few % in volume.
Discussion

The Au and Pt nano structures are of considerable interest. The effect of downsizing on the surface versus bulk atom ratio is worth of consideration. For example, in a 2 nm crystallite, the surface atoms amount to ~20-30 % of the total atoms depending on the geometry. Thus the nanostructure tends to minimize its surface energy and tends to contract slightly relative to its bulk lattice (induced by surface reconstruction, for example). The question is how it will have an effect on the s and d electron redistribution of which can be probed by the L\textsubscript{3,2} and M\textsubscript{3,2} – edge XANES. For both Au and Pt nano-crystallites, the experimental result indicates that Au nano-structure gains d charge and Pt nano-structure loses d charge (relative to the bulk). If there is no countervailing argument resulting from surface effects (reconstruction and interactions with adsorbates), our present calculation indicates that nano-Au favors s to d charge transfer marginally and nano Pt favors d to s rehybridization noticeably, for a 5% contraction of the lattice in both cases.

It must be noted, however, that the s-d rehybridization in these nominal full (Au) and nearly full (Pt) d band nano systems is very sensitive to surface effects which may involve surface d-band narrowing and additional net charge transfer from the adsorbate/substrate. Thus, Au-Si and Pt-Si interfacial interaction may have influenced our experimental results that suggest noticeable s-d charge redistribution in both nano Au and nano Pt. The calculation for Au suggests a marginal change, compared with Au on porous silicon in terms of whiteline behavior (nano Au exhibits a noticeable depletion in intensity) while the Pt calculation is in good accord with experiment. Thus our calculation suggests that the neglect of surface effect on the core of the nanostructure in the calculation may lead to less satisfactory results for nearly full d bands such as in Au and Ag. The surface will almost certainly contribute to the overall behavior observed in the experiment. Since there have not been sufficient systematic studies on the influence of surface on the electronic behavior of nano-crystallites, the trend revealed here should be used with caution especially for system with nearly full d bands which has very low densities of unoccupied d states above the Fermi level in the bulk to begin with.

Finally, it must be noted that although the usefulness of this calculation needs to be substantiated with further work, there is no doubt that the whiteline is extremely sensitive to the s-d hybridization caused by lattice compression/expansion both in experiment and calculation. Thus this kind of calculation/experiment will be very useful for studying the electronic structure of surface overlayers and the effect of pressure on s-d electron redistribution. One can envisage obtaining a correlation of whiteline intensity with the compressibility of s and d electrons, for example.

Conclusion

In summary, we have performed self-consistent calculations for fcc 5d metals including Au, Pt, Ir, and Re. The L\textsubscript{3} edge XANES spectra of nano Au and nano Pt are compared with bulk metals. They are shown to resemble those of bulk crystals with a slightly contracted lattice (~5% volume change), in the absence of surface effect. Our results of nano gold and nano platinum also indicate that these nano crystals essentially maintain their corresponding bulk properties but the nanosize has a small but noticeable effect on s-d rehybridization, especially on Pt, which has relatively localized unoccupied densities of state of d character at the Fermi level. It is also noted that the combined use of experiment and theory reported here could be used to study surface overlayers and pressure effects.

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