J. Synchrotron Rad. (1999). **6**, 315–316

L-edge XANES of 3*d*-transition metals

A. I. Nesvizhskii and J. J. Rehr

Department of Physics, Box 351560, University of Washington, Seattle, WA 98195-1560, USA

Using the new self-consistent, full multiple scattering FEFF8x code we calculate the XANES of the $L_{2,3}$ edges of Cu, Co, Ni, and other 3*d*-transition metals, ignoring many body effects other than extrinsic losses. To test the final state rule, we calculate the density of states and XANES with and without core hole. Remarkably, better agreement with experimental data is obtained when the calculations are done without a core hole. We observe a strong reduction of the calculated L edge white line strength when a full core hole is included. The difference in XANES of K edge spectra with and without core hole is much less pronounced.

Keywords: L-edge; XANES; core hole.

1. Introduction

X-ray absorption spectroscopy is a powerful tool for studying the electronic structure of solids. Now there is hope that X-ray Absorption Near Edge Structure (XANES) can became a reliable and direct way of obtaining local chemical information of complex and disordered materials. Many XANES calculations of metals have been done using band structure methods (Müller *et al.*, 1982; Ebert *et al.*, 1996) Although these calculations were successful in reproducing XANES spectra, they are of limited application because of requirements of lattice periodicity. In addition, these calculations often neglect core hole and self-energy effects and therefore do not allow direct comparison with experiment. At the same time, *ab initio* calculations of XANES using the FEFF7 code were complicated due to high sensitivity of the approach to the details of the scattering potential and slow convergence of the multiple scattering expansion in the near edge region.

In the present work we use the new self consistent FEFF8 code of Ankudinov *et al.* (1998). The major improvements of FEFF8 compared to FEFF7 are the self consistent calculation of the scattering potential and the implementation of an efficient real space multiple scattering method. The self consistent procedure accounts for charge transfer and gives a more accurate Fermi level position. The use of a full multiple scattering (MS) method for a cluster of a limited size is needed to avoid the poor convergence of the MS expansion for XANES. The code incorporates an energy dependent self-energy, so that the core hole life time and the energy dependent mean free path are calculated *ab initio*. This allows direct comparison with experiment without any additional broadening of calculated spectra. Also, the code does not require any lattice periodicity so it can be used for studying disordered and biological systems.

In this paper we study XANES of 3*d* transition metal L edges. To check the applicability of the final state rule (Von Barth & Grossman, 1979) we study the effect of a core hole on the absorption spectra, especially on position and intensity of the white line. This question is of importance for studying charge transfer, catalysis, and magnetic circular dichroism in these materials because the area under the white line can provide quantitative information about the number of unoccupied *d* holes at or above the Fermi level. In the absence of a core hole (the initial state rule), both the initial and the final states are represented by the ground-state single electron wave functions. In the presence of a core hole (the final state rule), the final state wave function is calculated for a system with a static core hole in given core level.

2. Results and Discussion

Results of the calculations are presented on Figs 1, 2, and 3. In Fig 1 we show the *s*, *p*, and *d* projected ground-state density for Cu. The size of the cluster is 125 atoms. The results are in excellent agreement with the results of full potential ground-state band structure methods (Eyert, 1997).

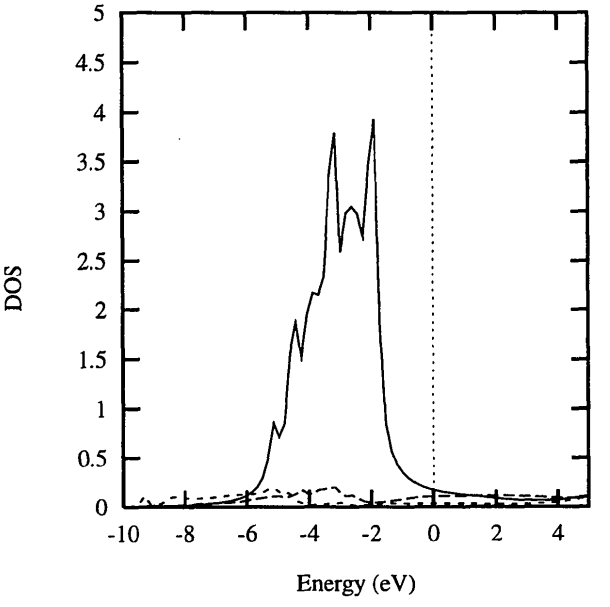

Figure 1
Projected density of states in Cu calculated without a core-hole. Solid line, long dashes, and short dashes correspond to the 3*d*, 3*p*, and 3*s* density of states respectively. The energy origin is at the Fermi level.

Results of calculations with and without a core hole and experimental data for $L2$ and $L3$ edges of Cu and Co are shown in Fig 2 and Fig 3 respectively. Better agreement with experiment (and with results of standard band structure calculations) is achieved when the calculations are done without a core hole. A characteristic feature of the experimental spectra of $L2$ and $L3$ edges of Cu and Co is a white line which originates from transitions to unoccupied d states. The calculations done without a core hole correctly reproduce both position and intensity of the white line, as well as general shape of $L3$ and $L2$ spectra. The inclusion of a core hole leads to an energy shift of the *d* density of states due to electron - core hole interaction. The shift of the Fermi level, however, is much smaller. As a result, we observe a strong reduction, or even absence, of the white line in XANES when a core hole is taken into account. At the same time the *p* density of states, which is much broader that the *d* density of states, is basically unaffected by the presence of a core hole. Consequently, the difference in XANES of K edge spectra with and without core hole is much less pronounced. We observed similar situations for other transition metals, though the effect of core hole becomes less dramatic for the transition metals with half filled or almost empty *d* band. However, we find that in

most cases the initial state rule is more favorable. We will not discuss here various reasons for the failure of the final state rule for $3d$ transition metals but it seems clear that a more realistic description of the core hole, as well as inclusion of many body effects, may be needed to resolve this discrepancy (see, for example, Stern & Rehr, 1983; Schwitalla & Ebert, 1998). We note that we did not vary the Fermi level position to obtain a better agreement with experiment, as it is often done with FEFF7.

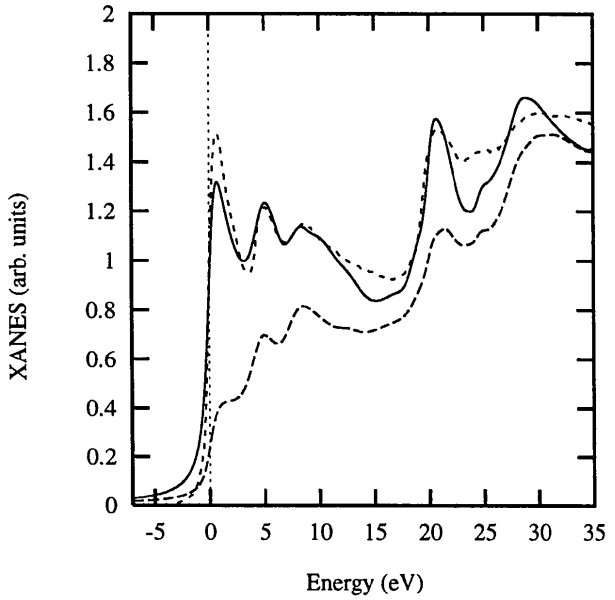

Figure 2
$L3$ and $L2$ edge XANES of Cu, solid line and long dashes represent the results of calculations without and with a core hole respectively, short dashes is experimental data taken from Ebert *et al.* (1996). The energy origin is at the $L3$ edge threshold.

We also analyzed the importance of multiple scattering on the density of states and XANES. We found that the size of the cluster needed to obtain reliable results for the scattering potential was typically less than 20 atoms (first and second neighbor shell). For the density of states and XANES, a cluster of about 100 atoms is usually sufficient to reproduce all significant details.

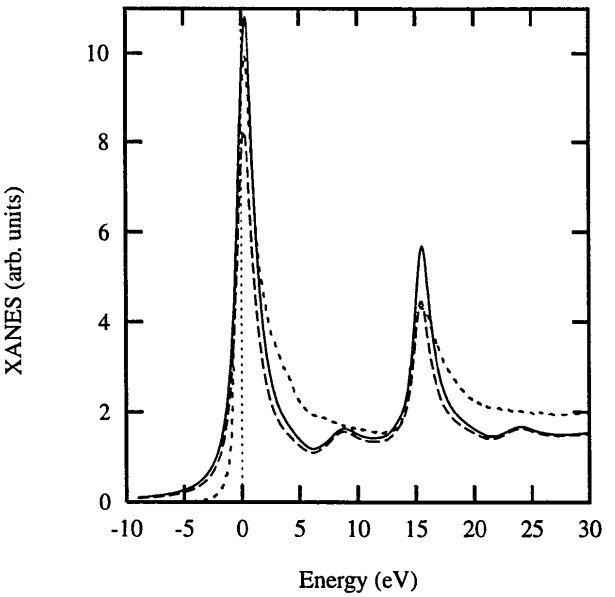

Figure 3
$L3$ and $L2$ edge XANES of Co, solid line and long dashes represent the results of calculations without and with a core hole respectively, short dashes is experimental data taken from Stohr (1997). The energy origin is at the $L3$ threshold.

We thank A.L. Ankudinov for helpful discussions and J. Stohr for providing the experimental data used in this work. The work was supported by DOE Grant DE-FG03-97ER45623/A000.

References

Ankudinov, A. L., Ravel, B., Rehr, J. J. & Conradson, S. D. (1998). *Phys. Rev.* B**58**, 7565–7576.
Ebert, H., Stohr, J., Parkin, S. S. P., Samant, M. & Nilsson, A. (1996). *Phys. Rev.* B**53**, 16067–16073.
Eyert, V. (1997). Electronic structure calculations for crystalline materials. In Michael Shringborg, editor, *Density Functional Methods: Application in Chemistry and Material Science*. Willey, Sussex.
Müller, J. E., Jepsen, O. & Wilkins, J. W. (1982). *Solid State Commun.* **42**, 365–368.
Schwitalla, J. & Ebert, H. (1998). *Phys. Rev. Lett.* **80**, 4586–4589.
Stern, E. A. & Rehr, J. J. (1983). *Phys. Rev.* B**27**, 3351–3357.
Stohr, J. (1997). Personal communication.
Von Barth, U. & Grossman, G. (1979). *Solid State Commun.* **32**, 645–649.

(*Received 10 August 1998; accepted 27 January 1999*)