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Topical Review

Comparison of theoretical and experimental Cu and Mo K-edge XAS

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ABSTRACT

We compare *ab initio* broad spectrum calculations of the K-edge X-ray absorption spectra of copper and molybdenum against accurate experimental measurements and tabulated standards on an absolute scale. Comparisons are also presented for the fine structure in the spectra.

1. Introduction

Accurate theoretical calculations of X-ray absorption spectra (XAS) are essential for quantitative interpretations of the spectra. While theoretical calculations of phase shifts and scattering amplitudes are widely used as standards for extended X-ray absorption fine structure (EXAFS) investigations [1], less attention has been devoted to XAS on an absolute scale over a broad energy range. Recently, however, there has been considerable interest in quantitative measurements of XAS [2]. Moreover there have been a number of theoretical developments [3–8] that call for a careful comparison with experiment. These developments include improved treatments of many-body effects which are implemented in the FEFF9.0 real-space multiple-scattering (RSMS) code [6], such as inelastic losses, core-hole effects, vibrational amplitudes, and the extension to full spectrum calculations of optical constants including solid state effects. There have also been improvements in the theory of the near-edge structure in XAS [7,8]. In view of these advances it is now useful to reassess the quality of modern calculations by comparing with absolute measurements [9–11] and tabulated atomic calculations [12,13].

In this work, we have used the *ab initio* XAS codes FEFF8.4 and FEFF9.0 to calculate both the K-edge EXAFS and XANES spectra of fcc Cu and bcc Mo, as well as the extended spectra over a broad range. The calculations are compared against absolute measurements of mass absorption and standard tabulations based on atomic codes [12,13]. In addition, a comparison of EXAFS fits was performed using the ATHENA and ARTEMIS EXAFS analysis codes [14].

2. Comparison of XAS in absolute units

A comparison of theory and high precision experiment in absolute units can provide a sensitive test of various assumptions in the theory. The FEFF9.0 calculations are based on Dirac–Fock calculations of the initial core-states together with a GW quasi-particle treatment of final, continuum states in the presence of a screened core-hole, where G is the photoelectron Green's function and $W=\varepsilon^{-1}v_{\mathrm{Coulomb}}$ is the screened coulomb interaction. At large energies, i.e., above a crossover energy E_x where Debye–Waller factors damp out the fine structure, solid state effects in the spectra are neglected. Detailed high-accuracy measurements of the mass absorption coefficient $\mu(E)/\rho$ of molybdenum [15] are presented in Fig. 1a. The scattering contributions were subtracted from the experimental data before comparison. This experimental data set had absolute point accuracies well below 0.1% and is one of the most accurate data sets currently available. Details of the experimental technique are given in the cited work and a review of the general principles is given in Ref. [16]. The statistical precision of the data was generally 0.02%. As shown in Fig. 1a, the full calculation of the XAS for Mo is in reasonable agreement with experiment over a broad spectral range. However, for both FEFF8.4 and FEFF9.0, the jump at the K-edge μ_0 and the amplitude of the XANES is smaller than that of the experimental data as seen in Fig. 1b. One source of this discrepancy appears to be the treatment of core-hole lifetime effects, which determines the shape of the threshold energy cutoff in the theory, and points to the need for improvements in the calculation of the background absorption cross-section $\mu_0(E)$. Another source of error near the edge is the neglect of the edge singularity effect of Mahan, Nozières, and De Dominicis (MND) [17–19]. Fig. 1c shows a comparison of calculations which include the MND effect (green) [20], calculations which do not include the effect (blue), and experiment (red). Qualitatively, the shape of the curve is improved when the MND effect is included, however, the

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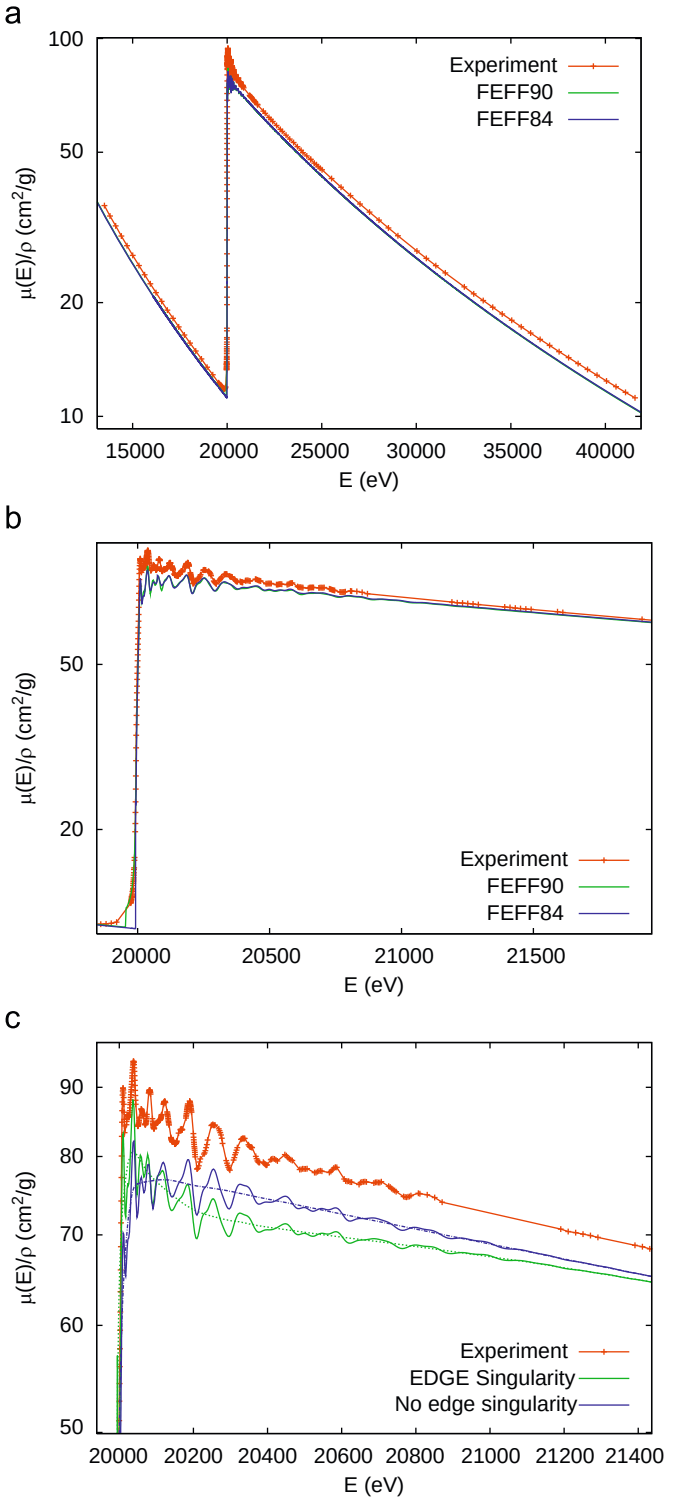

Fig. 1. Calculated mass absorption coefficient $\mu(\omega)/\rho$ at the Mo K-edge compared to experiment. (a) Shows a comparison of experiment (red) to FEFF8.4 (blue) and FEFF9.0 (green). Note that the calculated results are low by $\approx 3-4\%$ away from the edge, with the discrepancy becoming larger near the edge where the FMS and path expansion calculations are used. (b) Is the same as (a) except that the calculations have been multiplied by 1.03 in order to match the tails with experiment. Note that the disagreement is still large near the edge. Finally (c) shows calculations with (green) and without (blue) edge singularity effects compared to experiment (red). The atomic background calculations are shown as dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

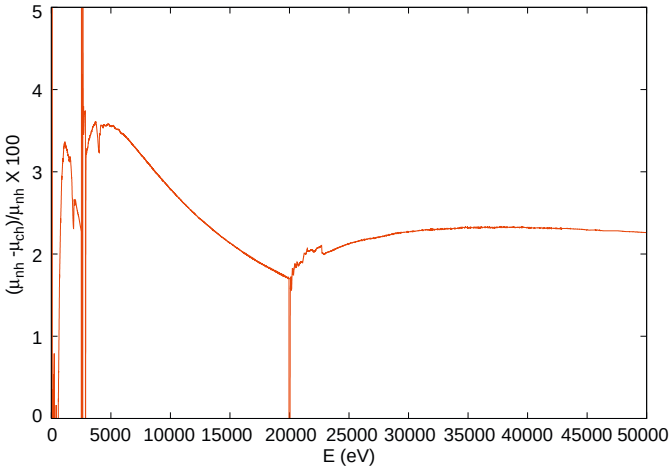

Fig. 2. Percent difference between calculations of $\mu(\omega)/\rho$ at the Mo K-edge with and without a core-hole. Note that the calculation with a core-hole is smaller by 2–4% over the whole spectral range, not including small regions near the edges.

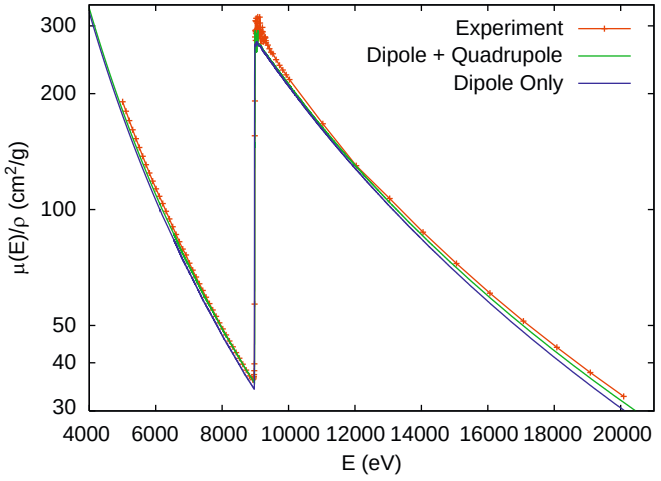

Fig. 3. $\mu(\omega)$ at the Cu K-edge. Two calculations which neglect fine structure are compared to experiment (red) over a broad energy range. The first calculation includes quadrupole transitions (green), while the second does not (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reduction in weight starting at $\approx 20\,100$ eV is unexpected and may point to problems in our implementation of this effect. We have also investigated the effect of the core-hole on the calculation, and found that including a core-hole in our calculation reduces the absorption by 2–4% over the whole spectral range as shown in Fig. 2. This suggests a problem with the treatment of the many-body amplitude reduction factor S_0^2.

Fig. 3 shows a comparison of experiment (red pluses) to a calculation which includes quadrupole transitions (green), and one which includes only dipole transitions (blue) effects. Both calculations neglect fine structure. Clearly quadrupole transitions are important for an accurate description of the high energy tail of the spectrum.

Finally, in order to investigate solid state effects on the spectrum we compare a simulated atomic absorption calculation with the *embedded atomic background* μ_0 of bulk Cu, i.e. a calculation which includes solid state effects in the potential, but does not include fine structure. The FEFF code requires at least two atoms for any calculation; thus we simulated the Cu atomic absorption by calculating the absorption of a Cu–He diatomic