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Single and multiple scattering XAFS Debye-Waller factors for crystalline materials using periodic Density Functional Theory

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Abstract. We present an accurate and efficient technique for calculating thermal X-ray absorption fine structure (XAFS) Debye-Waller factors (DWFs) applicable to crystalline materials. Using Density Functional Theory on a $3 \times 3 \times 3$ supercell pattern of MnO structure, under the nonlocal hybrid B3LYP functional paired with Gaussian local basis sets, we obtain the normal mode eigenfrequencies and eigenvectors; these parameters are in turn used to calculate single and multiple scattering XAFS DWFs. The DWFs obtained via this technique are temperature dependent expressions and can be used to substantially reduce the number of fitting parameters, when experimental spectra are fitted with a hypothetical structure. The size of the supercell size limits the R-space range that these parameters could be used. Therefore corresponding DWFs for paths outside of this range are calculated using the correlated Debye model. Our method is compared with prior cluster calculations and with corresponding values obtained from fitting experimental XAFS spectra on manganosite with simulated spectra.

1. Introduction

The X-ray Absorption fine structure (XAFS) \cite{1,2} is an essential tool for probing the structural and electronic properties of a material, which could be in crystalline form, amorphous or in solution. Structural information is typically obtained by the use of nonlinear least squares fitting of experimental extended XAFS (EXAFS) spectra with corresponding simulated spectra of a hypothetical structure. However, high fitting parameter correlation and multiple scattering (MS) may lead to erroneous structural information by EXAFS \cite{3}. MS appears in the EXAFS amplitude equation in the form of $e^{-2k^2\sigma_j^2}$, where $k$ is the photoelectron x-ray wavenumber and $\sigma_j^2$ is the mean square variation of the $j$th scattering path. This exponential term is called the EXAFS Debye-Waller factor (DWF). The $\sigma_j^2$ terms are direct functions of the sample’s vibrational normal mode spectrum properties (eigenfrequencies and eigenvectors) and temperature. When MS is substantial, as in the case of manganosite (MnO) due to the collinear Mn-O-Mn geometry, the number of available fitting parameters typically exceeds the maximum number of parameters data may support. The latter, given by the Nyquist theorem, is typically at the order of $2\Delta k\Delta R/\pi + 2 \cong 20–30$ parameters, where $\Delta k$ and $\Delta R$ are the effective k-space and R-space EXAFS.
spectra ranges, respectively [4]. For isotropic materials, these parameters may be sufficiently calculated using the correlated Debye model (DM), a single parameter model (Debye temperature) [5]. For anisotropic materials, such as MnO, Ressler et al. [6] observed that $\sigma_j^2$ single scattering (SS) parameters on Mn-O paths are overestimated by the correlated DM. This overestimation is typical for low Z elements. An improved fit was obtained by using two Debye temperatures, one for each element. However, the DWFs of MS scattering paths were obtained using ad hoc assumptions, such as approximating the MS DWF as a geometric average of DWF of constituent SS paths.

As an alternative to DM, SS and MS DWFs have been calculated by Poiarkova and Rehr using the force–field equation of motion method applied to Cu and Ge crystals [7]. Dimakis [8] presented a “hybrid” approach to calculate DWFs for MnO crystals. This approach combined nonlocal Density Functional theory (DFT) [9,10] phonon normal mode spectrum calculations on various MnO clusters (cDFT), which are used to obtain DWFs up to the available R-range as indicated by the cluster size. The remaining DWF parameters were calculated using the Debye model. In this work, we calculate the MnO DWFs from the phonon spectrum of its 3×3×3 supercell pattern via periodic DFT (pDFT). The main advantage of this method is the substantial increase of the effective R-range ($R_{\text{eff}}$), up to where DWFs are directly calculated via DFT. This avoids cluster size effects, which occurred in our previous report, where the $R_{\text{eff}}$ for cDFT was limited to 4.444 Å.

2. The MnO Phonon spectrum

The MnO crystal was modelled as a 3×3×3 supercell of the face-centred cubic model of the Fm3m space group, with a lattice parameter of 4.4448 Å [11]. Figure 1 shows the MnO unit cell, which is used in this work. All atoms are fixed in their crystallographic positions; lattice relaxation effects will be examined in a future work. Unrestricted DFT calculations were performed using the CRYSTAL06 [12] program that employs Gaussian type function basis sets centred at the atoms, and it has the capability of normal mode frequency estimation at the Gamma point ($k = 0$) [13]. The “modified” version of the nonlocal hybrid B3LYP functional was employed, which consists of the same exact and exchange functionals as the original B3LYP functional [14], paired with the VWN5 correlation functional [15]. The Mn innermost orbitals are described by effective core pseudopotentials [16]. The Mn atom effective valence basis set is described as follows: the original [6s5p3d2f1g] basis set by Martin et al. [17] is contracted to [4s3p2d] by dropping functions with exponents less than 0.1 and concurrently removing f and g functions from the original basis set. For oxygen, the [4s3p2d] basis set proposed by Valenzano et al. [18] was chosen and is optimized for the MnO calculations. SCF convergence is achieved by employing Anderson quadratic mixing [19] coupled with additional mixing of the occupied with the virtual orbitals. The $\sigma_j^2$ terms are calculated using the output CRYSTAL06 frequency calculation file and expressed as a function of temperature.
3. Results and Discussion

Table 1 shows the SS and MS $\sigma^2$ values for MnO calculated via pDFT, cDFT and the DM at 300 K. Additionally, the $\Delta\sigma^2 = \sigma^2_{p\text{DFT}} - \sigma^2_{\text{best}}$ is also reported. Figure 2 shows the EXAFS Fourier transformed results of theoretical calculations to the experimental MnO spectra. The spectra range in k-space is 2–11.7 Å⁻¹, whereas the fit range in R-space is 0.86–6.35 Å. The fit on figure 2 was obtained using the IFEFFIT [19] program as follows: All DWFs were calculated via pDFT and thus eliminated from the fitting parameter list, with the exception on some paths as shown in table 1. R$_{eff}$ was not used in the fitting process since it did not affect the fit quality. The $E_0$ shifts, one for each element, has been manually

<table>
<thead>
<tr>
<th>Path</th>
<th>N</th>
<th>R(Å)</th>
<th>$\sigma^2$ (×10⁻³ Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pDFT</td>
<td>cDFT</td>
<td>DM $^a$</td>
</tr>
<tr>
<td>Mn-O</td>
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<td>2.222</td>
<td>9.34 10.07</td>
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<tr>
<td>Mn-O</td>
<td>48</td>
<td>3.794</td>
<td>11.86 13.34</td>
</tr>
<tr>
<td>Mn-O</td>
<td>8</td>
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<td>19.00 13.70</td>
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<tr>
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<td>4.445</td>
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<td>Mn-O</td>
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<td>4.969</td>
<td>24.79 $^b$</td>
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<td>Mn-O-Mn</td>
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<tr>
<td>Mn-Mn</td>
<td>24</td>
<td>5.444</td>
<td>10.09 $^b$</td>
</tr>
</tbody>
</table>

$^a$ SS values are from [7].

$^b$ Not reported by [9] due to finite cluster size.

Figure 2. a) Magnitude and b) imaginary part of EXAFS Fourier transformed results of theoretical calculations to the experimental MnO spectra at 300K. The Debye model was used for MS paths with $R_{eff} = 6.666$ Å as in Ref. [8].
inputted as constants to avoid parameter correlation. Coordination numbers and the $S_0^2$ amplitude reduction parameter were kept fixed during the fitting process. However, the coordination numbers of two scattering paths, the SS and DS Mn-Mn paths at $R_{\text{eff}} = 4.445$ Å were reduced to 55%. This is attributed to either Jahn-Teller distortions [20] of the MnO$_6$ octahedral, or to the presence of a dihedral angle between successive MnO$_6$ octahedra of less than 180°. The latter effect had been reported [7]. Using the $\sigma^2$ values the fit agrees well with the experimental spectra. The pDFT method calculates $\sigma^2$ values at an overall acceptable accuracy for EXAFS data analysis. However, cDFT and the DM may provide better accuracy for some particular paths (e.g., the first shell Mn-O path). The $\sigma^2$ values obtained via pDFT may be improved by performing calculations in a denser Monkhorst-Pack grid [21] (i.e., current grid is $4 \times 0 \times 4$), which requires increased CPU and storage space.

4. Conclusion
SS and MS DWFs have been directly calculated from the phonon normal mode spectrum of the $3 \times 3 \times 3$ MnO supercell using pDFT. The pDFT method is more advantageous than the prior cDFT method, where the accuracy of latter suffered due to the finite cluster size. This method is generic and will be expanded in other crystalline materials.

5. References
[19] Newville M 2001 J. Synchrotron Rad. 8 322