Single and multiple scattering XAFS in $BaZrO_3$: a comparison between theory and experiment

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Abstract

A comparison between theory and experiment is made for the XAFS of the Zr and Ba K-edges in $BaZrO_3$. $BaZrO_3$ is chosen because of its simple and well understood structure but combines metallic atoms with oxygens. It is found that adding phase corrections to the theoretical XAFS significantly improves the accuracy of the structural parameters. These corrections are changes in the core electron threshold energy E_0 for each single scattering path involving a different type of backscattering atom. This, together with the fact that no corrections were needed for pure metal Cu , suggests that the phase corrections needed are due to charge distribution effects which are neglected in the theory.

I. INTRODUCTION

Theoretical standards are currently widely used in XAFS analysis, both because of recent improvements in the theoretical computational codes available as well as due to the lack of good experimental standards in many cases of interest, especially when multiple scattering (MS) is important.

In this work, FEFF5[1], a MS XAFS code was used for calculating the theoretical XAFS in $BaZrO_3$. $BaZrO_3$ has a fairly simple and well known structure (ideal perovskite) and thus is a good structure to check the theory against.

II. ANALYSIS AND RESULTS

Zr K-edge XAFS data at 10, 100 and 200 K were obtained from the experimental absorption data after removing the single atom absorption background using the program AUTOBK[2]. The separation of the background is done by minimizing the difference between the Fourier transformed XAFS and a standard (in this case the theoretical XAFS) for $r \leq 1$ Å. The theoretical XAFS was calculated using the FEFF5 code on a $BaZrO_3$ cluster with the lattice parameter being that obtained by extrapolating lattice constant measurements at room temperature and above to 200 K[3]. The fitting of the data was done in r-space up to $r = 4.5$ Å. Fourier transform parameters and the r and k range used in the fitting are listed in Table I. Only single scattering (SS) and collinear MS paths (listed in Table II) were found to contribute significantly to the total XAFS in this fitting range. Initially, the following parameters in the XAFS expression of each path were allowed to vary: ΔE_0, a shift to the energy origin; ΔR_i, a change in equilibrium bond lengths; σ_i^2, Debye-Waller factors; S_0^2, a passive electrons amplitude reduction factor set to be equal for all paths as it depends only on the central atom. S_0^2 and ΔE_0 were set to be temperature independent. The σ_i^2 factors for the MS paths can be related to the SS ones by a simple average, decreasing the number of parameters needed. Fig. 1 shows the fitting results obtained by using an overall ΔE_0 for all paths. Fig. 2 shows the temperature dependence of the equilibrium bond lengths. The distances obtained are not consistent with any reasonable extrapolation of the x-ray diffraction data above room temperature, even if anharmonicity is included. The phase shifts for the center and backscattering atoms, δ_e and δ_b, respectively, are calculated by FEFF based on an overlapping relativistic-atom muffin-tin potential model. This model neglects charge transfer since it uses a sum of *neutral* atomic potentials. These chemical effects can be approximately compensated for by a change in the energy reference for each path[4]. For the case here, it is sufficient to give a different ΔE_0^i to each SS path involving a different type of backscattering atom and for the MS paths, an average was done using the ΔE_0^{i}'s of the SS paths, the weight given by the number of times the photoelectron 'visits' each backscattering atom. Thus the MS paths do not add any further ΔE_0 parameters, important because the number of degrees of freedom in the data is limited. If the SS path $Zr_c \rightarrow O \rightarrow Zr_c$ has ΔE_0^1 and $Zr_c \rightarrow Zr \rightarrow Zr_c$ has ΔE_0^2, then the MS paths $Zr_c \rightarrow O \rightarrow Zr \rightarrow Zr_c$ and $Zr_c \rightarrow O \rightarrow Zr \rightarrow O \rightarrow Zr_c$ will have $(\frac{1}{2}\Delta E_0^1 + \frac{1}{2}\Delta E_0^2)$ and $(\frac{2}{3}\Delta E_0^1 + \frac{1}{3}\Delta E_0^2)$, respectively.

Fig. 1 shows the fitting obtained by means of this procedure. The new distances obtained are shown in Fig. 2. The quality of fit increased by more than 50%, even accounting for the increased number of parameters, and the physical parameters obtained are in agreement with the diffraction data. The values obtained for the ΔE_0^{i} are listed in Table II. Their *relative* signs and values contain information about the sign, amount of charge transfer between atoms, and angular dependence of the interstitial charge density. This will be addressed in a forthcoming paper[5]. Ba K-edge results are consistent with the Zr edge results and for reasons of space are not included in this paper.

III. CONCLUSIONS

It was shown that E_0 corrections are needed for the phase shifts calculated by FEFF in order for the physical parameters extracted from the data to be more accurate. These corrections, though small, are significant and should be added in cases where charge transfer plays an important role.

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TABLES

TABLE I. Fitting regions and Fourier transform parameters.

Edge	r_{min} (Å)	r_{max} (Å)	k_{min} (Å^{-1})	k_{max} (Å^{-1})	kw	dk (Å^{-1})
Zr	1.2	4.5	3.5	14.5	2	1.5

TABLE II. Paths used in the fitting and values obtained for the $\Delta E_0^{\rm i}$. The c suffix indicates the position of the central atom in the path.

Path	Overall ΔE_0	$\Delta E_0^{\rm i}$
$Zr_c \rightarrow O \rightarrow Zr_c$	-0.8 (0.3)	-0.7 (0.3)
$Zr_c \rightarrow Ba \rightarrow Zr_c$	-0.8 (0.3)	-1.6 (0.4)
$Zr_c \rightarrow Zr \rightarrow Zr_c$	-0.8 (0.3)	2.5 (0.6)
$Zr_c \rightarrow O \rightarrow Zr \rightarrow Zr_c$	-0.8 (0.3)	0.9 (0.3)
$Zr_c \rightarrow O \rightarrow Zr \rightarrow O \rightarrow Zr_c$	-0.8 (0.3)	0.4 (0.3)
$Zr_c \rightarrow O \rightarrow Zr_c \rightarrow O \rightarrow Zr_c$	-0.8 (0.3)	0.4 (0.3)
$Zr_c \rightarrow O_{far} \rightarrow Zr_c$	-0.8 (0.3)	-0.7 (0.3)

FIGURES

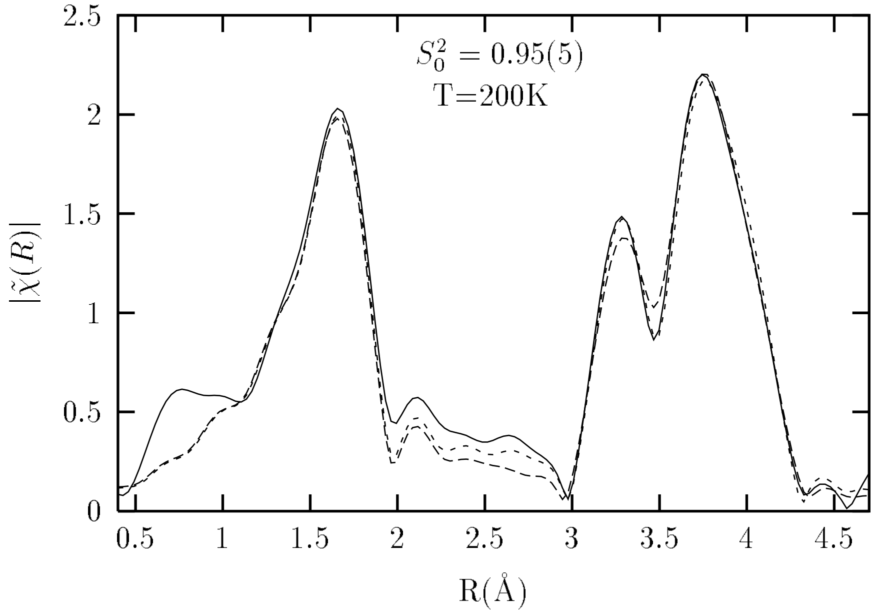

FIG. 1. Zr K-edge fitting results. Solid lines: data; Long Dashes: theory using an overall ΔE_0; Short Dashes: theory using ΔE_0^{i}.

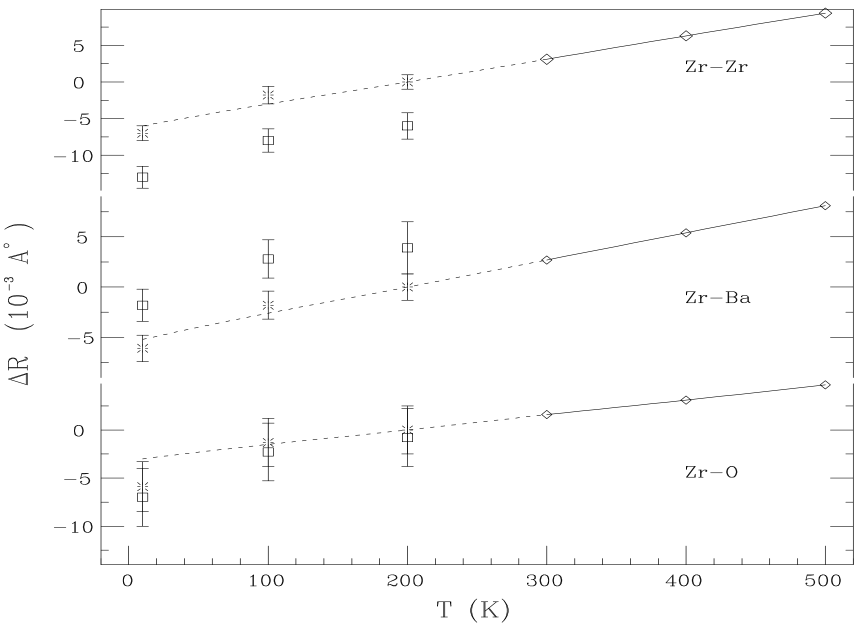

FIG. 2. Temperature dependence of the equilibrium bond lengths obtained in the fitting. Changes are relative to x-ray diffraction data at 200 K. Diamonds: x-ray diffraction data; Dashes: linear extrapolation of diffraction data; Squares: using overall ΔE_0; Stars: using ΔE_0^{i}.