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Comparison of Spinel and Monoclinic Crystal Structures of γ-Al_2O_3 for Simulation of Electron Energy Loss Spectra

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γ-Al_2O_3 is one of the metastable polymorphs of alumina that is used in many applications, such as in adsorbents and catalyst supports [1]. However, an accurate description of the crystal structure of γ-Al_2O_3 is still being disputed. Early studies of the structure of γ-Al_2O_3, including the seminal study by Zhou and Snyder [2], determined γ-Al_2O_3 has a spinel structure similar to the structure of $MgAl_2O_4$. As there are fewer cations in γ-Al_2O_3 per unit cell than $MgAl_2O_4$, some of the cation positions are vacant to satisfy stoichiometry. Recently, theoretical studies have suggested non-spinel structures as the more accurate structural description of γ-Al_2O_3, the most commonly cited of which was given by Digne et al. [3]. These theorists combined molecular dynamics (MD) and density functional theory (DFT) calculations to simulate the thermal dehydration of boehmite to γ-Al_2O_3, which is the most common synthesis method of γ-Al_2O_3. They predicted that the γ-Al_2O_3 structure was distorted into a monoclinic unit cell. Although subsequent experimental studies suggest that the spinel model is the more accurate structural description [4], it is also more computationally intensive to use in simulations because of the partial occupancy of the cation sites. As a result, the monoclinic model of γ-Al_2O_3 is commonly used in simulations, including of the electronic properties. Gauging the accuracy of this approach has been complicated by the nature of γ-Al_2O_3 produced by the dehydration of boehmite, which usually exhibits poor crystallinity and significant amounts of impurities. This has hindered the ability to directly compare experimental results with simulations, which uses simple, well-defined structures for input.

In this study, we compared the two structures using combined experimental and simulated electron energy-loss spectroscopy (EELS). EELS provides information on both local composition and electronic structure. To overcome the issue of sample non-ideality, we grew well-defined single-crystal γ-Al_2O_3 (111) thin films through the controlled oxidation of NiAl (110). TEM cross-sectional samples of the γ-Al_2O_3 thin film were prepared using a focused ion beam (FIB). The γ-Al_2O_3 thin film was characterized using XRD, TEM and SAED. The EELS spectra were compared to simulated O-K and Al-$L_{2,3}$ EELS spectra of bulk γ-Al_2O_3 calculated using the FEFF9 code. The FEFF simulations were performed using both the monoclinic model and the spinel model with varying cation vacancy distributions.

XRD confirmed the growth of single crystal γ-Al_2O_3 (111). SAED spot patterns of the γ-Al_2O_3 show the symmetry of the cubic fcc spinel structure (Figure 1) [5]. The calculated d-spacings from the SAED (Figure 1b) pattern match the d-spacings from the spinel γ-Al_2O_3 to within 3% error. The FEFF simulated EELS spectra of different γ-Al_2O_3 models do not show clear discerning features (Figure 2) [5]. This can be explained by the similarity in atom coordination and nearest neighbors between the two models. According to these results, the monoclinic model is sufficiently close chemically and electronically to the defective spinel – the more accurate structural model – for use in simulations [6]. Having this assurance

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of the accuracy of using the monoclinic model, we can apply it to EELS simulations of Pt/γ-Al_2O_3, which is an important and widely studied industrial catalyst.

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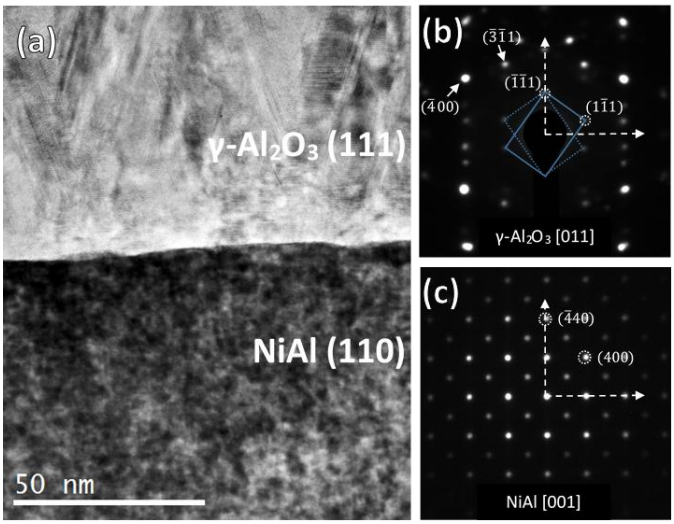

Figure 1. TEM image of NiAl/γ-Al_2O_3 interface (a) and the corresponding indexed SAED patterns from both materials (b, c) [5].

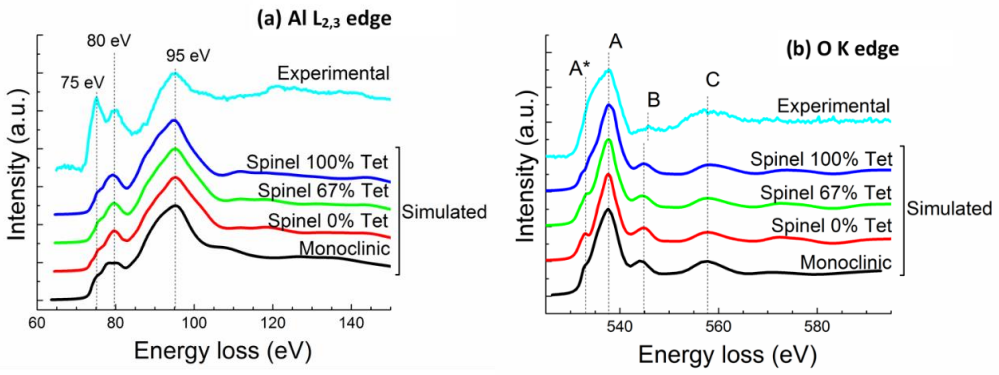

Figure 2. Comparison of the bulk Al_2O_3 experimental EELS and FEFF simulations of Al $L_{2,3}$ (**a**) and O K (**b**) spectra. The near-edge spectral features compared between the experiments and simulations are indicated by dashed lines [5].

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