

Hyperfine electric field gradients and local distortion environments of octahedrally coordinated Fe²⁺

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ABSTRACT

We report ab initio electronic structure calculations that directly relate given local chemical and distortion environments to corresponding hyperfine electric field gradients (EFGs) in ⁵⁷Fe Mössbauer spectroscopy, thereby giving needed interpretive power to the technique in characterizing ^{VI}Fe²⁺ environments in minerals. Changes of the EFG with various distortions were investigated on model clusters, including the bare octahedra FeO₆¹⁰⁻ and Fe(OH)₆⁴⁺, and various seven-octahedra sections of an octahedral sheet, through self-consistent charge X α ab initio calculations. Distortions examined for all clusters were flattening, counter-rotation, and bond scaling, as well as changes in neighbor bond lengths and the identity and ordering of neighbor cations for the seven-octahedra clusters. The evolution of the EFG with distortion was derived at $T = 0$ K and $T = 300$ K as a function of the distortion parameters. We find that the percent change in the EFG over the range of distortion parameters found in 1M trioctahedral micas is greatest with flattening for the clusters compared, suggesting that flattening is the most important structural distortion in determining the EFG. The EFGs for the seven-octahedra cluster as a function of flattening were compared for thirteen configurations of Mg²⁺ and Al³⁺ cations in the first nearest-neighbor octahedra. The percent change in the EFG for flattening and cation substitution was found to be of similar magnitude. In comparing EFG vs. flattening curves with measured quadrupole splitting distributions (QSDs), the magnitudes of EFGs in the theoretical curves agree well with experiment. The sharp high quadrupole splitting edge is explained by the presence of a maximum in the EFG vs. flattening curve. These model calculations are a necessary first step in establishing a firmer link between local structural distortions in minerals and measured QSDs.