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Wave vector and field vector orientation dependence of Fe *K* pre-edge X-ray absorption features in clinopyroxenes

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Abstract

Pre-edge X-ray absorption features are commonly used to derive redox states for transition metal oxides in crystals and glasses. Several calibrations for Fe^{2+} and Fe^{3+} in silicate glasses have utilized the general relationships among pre-edge peak intensity, energy, and redox state. However, absorption variations complicate those relationships in anisotropic crystals. Although absorption anisotropy at and above the energy of the rising edge adheres to the typical $\cos^2$ relationship observed in absorption spectroscopies at other energies, the anisotropy of the pre-edge is far more complicated. Prior studies focusing on pre-edge absorption anisotropy demonstrate a 1-cos4φ dependence of absorption magnitudes with rotation. Experiments presented here show that absorption magnitudes of the pre-edge vary as a function of both electric field vector orientation and wave vector direction. However, rotations around the field vector axis or wave vector axis individually result in $\cos^2$ dependence of absorption magnitudes. Rotations where both wave vector and field vector orientation are varied are not well fit by either model in the pre-edge. The resulting anisotropy complicates the process of measuring characteristic absorption in the pre-edge, making valence state determinations challenging for strongly anisotropic crystal structures such as pyroxene.

Keywords: X-ray, absorption, anisotropy, pre-edge, clinopyroxenes, ferric