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The absorption indicatrix as an empirical model to describe anisotropy in X-ray absorption spectra of pyroxenes

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Abstract

Anisotropic absorption in crystals is routinely observed in many spectroscopic methods and is recognized in visible light optics as pleochroism in crystalline materials. As with other spectroscopies, anisotropy in Fe *K*-edge X-ray absorption spectroscopy (XAS) can serve both as an indicator of the general structural arrangement and as a conundrum in quantifying the proportions of absorbers in crystals. In materials containing multiple absorbers, observed anisotropies can typically be represented by a linear relationship between measured spectroscopic peak intensities and relative absorber concentrations. In this study, oriented XAS analysis of pyroxenes demonstrates that the macroscopic theory that describes visible light absorption anisotropy of triaxially anisotropic materials can also be applied to X-ray absorption in pyroxenes, as long as the orientation and magnitude of the characteristic absorption vectors are known for each energy. Oriented single-crystal XAS analysis of pyroxenes also shows that the measured magnitude of characteristic absorption axes at a given orientation is energy-dependent and cannot be reproduced by linear combination of intermediate spectra. Although the macroscopic model describes a majority of the anisotropy, there is distinct discordance between the observed and interpolated spectra in the pre-edge between 7109 and 7115 eV, which is marked by spikes in RMSE/mean intensity ratio. Absorption indicatrices for samples analyzed in the visible and at X-ray wavelengths are modeled with a three-dimensional (3D) pedal surface, which functions as an empirical way of interpolating between the observed absorption data. This surface only requires a maximum of three coefficients, and results from the summation of 3D lemniscates. An absorption indicatrix model can be used to characterize anisotropic absorption in crystals and provides a way of comparing XAS spectra from randomly oriented crystals, such as those from polished sections, to a database of characterized crystals.

Keywords: Pyroxene, XANES, anisotropy, absorption, indicatrix