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Hyperfine electric field gradient tensors at Fe^{2+} sites in octahedral layers: Toward understanding oriented single-crystal Mössbauer spectroscopy measurements of micas

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Abstract

In this first systematic, theoretical study of the complete electric field gradient (EFG) tensor of ^{57}Fe Mössbauer spectroscopy as a function of chemistry and local structural distortion using electronic structure calculations, local EFG tensors were calculated at the central Fe^{2+} sites in clusters of seven octahedra, where the neighbor octahedra were populated with a mixture of Mg^{2+} and Al^{3+} cations. The independent parameters of the EFG tensor—particularly the principal value V_{ZZ}, the asymmetry parameter η, and the direction of the principal axis with regards to the octahedral sheet—were examined in detail as functions of octahedral flattening for each of the thirteen possible configurations of cations. We demonstrate that the argument that the EFG tensor at a particular site is largely determined by the point group symmetry of the corresponding crystallographic site is not correct. We find that in clusters with monoclinic or triclinic local point group symmetry, the value of V_{ZZ} changes discontinuously from positive to negative as flattening increases. The principal axis changes from being in the plane of the octahedral sheet to being normal to it at this discontinuity, and the value of η reaches a maximum and begins to decline. This discontinuous behavior is caused by the continuous change of the EFG eigenvalues as the Fe(3*d*) character of the highest occupied spin-down orbital evolves with flattening. Taking EFG tensor results from all clusters, and using probabilities for the occurrence of each possible cation configuration in a chemically disordered octahedral sheet of a given bulk composition, we simulate averages and distributions of η, principal axis angles, and quadrupole splittings. While the value of η is broadly distributed from zero to one at all flattening angles and bulk compositions, there are two distinct populations of principal axes, normal to and in-plane with the octahedral sheet, as has been observed experimentally. We find these in-plane and normal populations of principal axes correspond exactly to populations with positive and negative values of $V_{ZZ,}$ respectively. Histograms representing quadrupole splitting distributions (QSDs) show features found in experimental QSDs, such as a constant high edge, a variable low edge, and a QSD width that changes dramatically with flattening. These results represent the first predictions relating average structural parameters, as would be obtained by X-ray diffraction, to characteristics of the Fe^{2+} QSD, as obtained by ^{57}Fe Mössbauer spectroscopy, in a chemically disordered material.