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 $\eta$, 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 $\eta$ reaches a maximum and begins to decline. This discontinuous behavior is caused by the continuous change of the EFG eigenvalues as the Fe(3d) 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 $\eta$, principal axis angles, and quadrupole splittings. While the value of $\eta$ 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.

INTRODUCTION

Structural and chemical information can only be extracted from Mössbauer spectra to the extent that the measured hyperfine parameters can be linked to corresponding crystal-chemical features by relations such as those obtained through ab initio electronic structure calculations. The indirect nature of any such hyperfine method, where crystal chemical features affect the measured nuclear resonances only through the local electronic structure, is probably the greatest barrier to the more widespread use of $^{57}$Fe Mössbauer spectroscopy in materials science and mineralogy (Rancourt 1998). The present paper is part of a continuing effort (Evans 2001; Evans et al. 2005) to bridge the gap between the measurement of hyperfine parameters and the determination of the corresponding crystal-chemical features of a mineral.

We feel it is essential to acknowledge and treat the intrinsic disorder of a particular sample, rather than to only calculate the electronic structure corresponding to the average unit cell, as is generally done (e.g., Tossell et al. 1974; Terra and Ellis 1997, 1998; Lougear et al. 2000). Only in this way can the distributions of hyperfine parameters measured using Mössbauer spectroscopy be properly interpreted and exploited (Rancourt 1994; Rancourt et al. 1994). This is the first study that explicitly considers how different local distortion environments produce different kinds of electric field gradient (EFG) tensors.

In a previous paper (Evans et al. 2005) we presented the results of hyperfine EFG calculations at the Fe$^{2+}$ nucleus in FeO$_{11-}$-centered clusters, focusing primarily on that component of the electric field gradient tensor which is proportional to the quadrupole splitting observed in random powder absorber Mössbauer spectroscopy. The current work focuses on the other independent components of the EFG tensor, which can be determined through oriented single-crystal Mössbauer spectroscopy, the asymmetry parameter $\eta$, and the directions of the EFG eigenvectors.