The Electric Field Gradient In Synthetic Fayalite (A Supplement)

Werner Lottermoser[1], Sven-Ulf Weber[2], Armin Kirfel[3]
[1] Paris-Lodron-University, Dep. of Materials Engineering and Physics, Salzburg, Austria
[2] Univ. of Technology, Inst. of Physical and Theoretical Chemistry, Braunschweig, Germany
[3] University of Bonn, Steinmann Inst. of Geology, Mineralogy and Paleontology, Germany

The electric field gradient (EFG) tensor is a central quantity when studying the relationship between structural and chemical properties in solids because it provides a most sensitive measure for the size and shape of the electric charge distribution around a given nucleus on a certain crystallographic site. Especially in case of low site symmetries the evaluation of this tensor with regard to its direction and magnitude is non-trivial but strongly correlated with other physical properties. Experimentally, the EFG is determined by Mössbauer spectroscopy yielding the quadrupole splitting Δ. Additionally, from single crystal spectra the asymmetry parameter $\eta = (V_{XX}-V_{YY})/V_{ZZ}$, representing the rhombic distortion of the EFG-ellipsoid, can be obtained, as well as the orientation of the EFG-tensor with respect to the crystallographic axes from the intensity distribution of the Mössbauer peaks with two angle parameters β and α (see, e.g., Gonser 1975). Theoretically, the EFG-tensor is derived from electronic structure calculations in the local density approximation (Grodzicki 1980). This is commonly regarded as the state-of-the-art treatment of large systems, i.e. with about 100 atoms per unit cell. A third method to derive the EFG tensor has been developed in our group (semi-quantitative approach). It uses the deformation electron densities (DED) ρ as derived from X-ray or synchrotron diffraction data and produces four-dimensional hyperareas dependent on their cartesian coordinates x,y,z as floating in space with the functional value of ρ being shown as transparency of the chosen colour (opacity). In this program system, it is possible to click on the relevant density hyperareas and to integrate them over their volume in space. Using a point charge formalism the EFG resulting from these integrated hyperareas is automatically calculated with resulting eigenvectors and eigenvalues together with a screen plot for control purposes.
The methods mentioned above had been applied to several compounds in the past, in particular synthetic fayalite α-Fe_2SiO_4 (Lottermoser et al. 2002). There, the evaluation of the EFG was quite successful yielding cluster sizes of up to 97 atoms around the two crystallographically non-equivalent iron sites with the exception of the semi-quantitative approach where in particular the azimuthal components of the EFG were not well met. Using the very accurate synchrotron structure data by A. Kirfel with a R-value of 0.6% and a sophisticated version of our DED program, however, it was now possible to achieve an overall agreement between calculated and experimental EFG orientations of a few percent.

Acknowledgements: Financial support of the Austrian Fund for Scientific Research (FWF) under the grant number P18329-N20 is gratefully acknowledged.

References:
Gonser U. (1975), In: U. Gonser (Ed.), Topics in Applied Physics, vol. 5, Springer, Berlin-Heidelberg-New York, 1-51.
Grodzicki M. (1980), J Phys, B13, 2683-2692.
Lottermoser W., Steiner K., Grodzicki M., Jiang K., Scharfetter G., Bats J.W., Redhammer G.J., Treutmann W., Hosoya S., Amthauer G. (2002), Phys Chem Minerals, 29, 112-121.