

⁵⁷Fe Mössbauer-effect studies of Ca-rich, Fe-bearing clinopyroxenes: Part III. Diopside

EDDY DE GRAVE^{1,*} AND SIGRID G. EECKHOUT^{1,2}

¹Department of Subatomic and Radiation Physics, Ghent University, B-9000 Gent, Belgium

²Department of Geology and Soil Science, Ghent University, B-9000 Gent, Belgium

ABSTRACT

Three natural Fe-bearing diopside samples, hereafter labeled Dp1, Dp2, and Dp3, have been examined by Mössbauer spectroscopy at temperatures from 4.2–800 K. The Fe contents are 0.01, 0.06, and 0.30 atoms per formula unit (apfu), respectively. All three species contain some Fe in the trivalent state. The spectra are adequately described by a superposition of three quadrupole doublets arising from Fe²⁺(M1), Fe²⁺(M2), and Fe³⁺. The Fe³⁺ fraction seems to increase with increasing total Fe. The coordination of the ferric ions could not be inferred, but the observed line broadening of the Fe³⁺ doublet indicates that they possibly substitute at both M1 and M2. The ferrous ions have a strong preference for the M1 sites. For the ferroan diopside sample Dp3 a spectrum at 80 K in an applied field of 60 kOe was recorded to determine the signs and the asymmetry parameters of the electric-field gradient. The signs are all negative and the asymmetry is large (~0.9), implying that an additional distortion is superimposed on the trigonal compression of the polyhedra. The center shifts δ for the two Fe²⁺ sites are equal within experimental error limits. From their temperature variations, equal values for the lattice temperatures, Θ_M , and hence for their recoilless fractions, f_2 , at any given temperature have been deduced. The recoilless fraction, f_3 , for Fe³⁺ is higher. The f_2/f_3 ratio was found to be ~0.95 at 80 K, and decreases with increasing temperature. The temperature variations of the ferrous quadrupole splittings show the importance of spin-orbit coupling. They were calculated from the thermal populations of the 25 electronic levels within the ⁵D term. The energies of these levels were determined by diagonalization of the complete crystal-field Hamiltonian. For the numerical expression of this Hamiltonian, use was made of the point-charge approach, which takes into account the real point symmetry of the M1 and M2 lattice sites by considering the positions and the effective charges of the various cations and anions in the diopside unit cell. The lattice contribution to the electric-field gradient and the spin-orbit coupling were included. We found that this theoretical treatment yielded excellent results for the M1 sites, correctly predicting the temperature dependencies of the quadrupole splittings for all three diopside species and the high magnitude of the asymmetry parameter. In contrast, the analyses for the M2 sites were less successful. We argue that the failure is due to a lack of correct crystallographic data concerning the coordination of Fe²⁺ at M2 in diopside.