American Mineralogist, Volume 88, pages 1129–1137, 2003

^{57}Fe Mössbauer-effect studies of Ca-rich, Fe-bearing clinopyroxenes: Part I. Paramagnetic spectra of magnesian hedenbergite

SIGRID G. EECKHOUT[1,2,*] AND EDDY DE GRAVE[2]

[1]Department of Subatomic and Radiation Physics, Ghent University, B-9000 Gent, Belgium
[2]Department of Geology and Soil Science, Ghent University, B-9000 Gent, Belgium

ABSTRACT

Mössbauer spectra (MS) of two natural magnesian hedenbergite samples (hereafter HED1 and HED2) were collected at temperatures in the range 35 to 800 K. At selected temperatures a longitudinal external field of 60 kOe was applied to the absorbers. The samples were observed to order magnetically at $T_N = 33 \pm 1$ K and 27 ± 1 K, respectively. The temperature dependencies of the Fe^{2+} center shifts, δ, were analyzed using the Debye model for the lattice vibrations, including a temperature variation for the intrinsic isomer shift, δ_I. The characteristic Mössbauer temperatures, Θ_M, of HED1 and HED2 were found to be 440 ± 20 K and 490 ± 20 K, and the intrinsic isomer shifts, δ_I, to be 1.434 ± 0.005 mm/s and 1.440 ± 0.005 mm/s, respectively, with a linear correlation coefficient, a, between δ_I and T of -4.5×10^{-5} mm/sK. From the external-field (60 kOe) MS recorded at 83, 147, 223, and 277 K for HED2, the principal component of the electric field gradient (EFG), V_{zz}, is determined to be positive and the asymmetry parameter $0.70 \leq \eta \leq 0.80$. Considering the discrepancy between the calculated and experimental applied-field MS, the obtained results for HED1 are assumed to be somewhat less accurate. The temperature variations of the quadrupole splitting, $\Delta E_Q(T)$, have been interpreted using the crystal-field model. Two approaches have been applied to evaluate the crystal field. In both cases the crystal-field Hamiltonian included the spin-orbit coupling. The first model emanates from the approximate and simplified symmetry of the ferrous sites, whereas the second takes into account the real symmetry of the sites, thus leading to a point-charge calculation. The temperature variations $\Delta E_Q(T)$ and $\eta(T)$ could be successfully described using the latter approach.