Magnetic properties of synthetic $P_2_1/c$ (Mg-Fe)SiO$_3$ clinopyroxenes as observed from their low-temperature Mössbauer spectra and from SQUID magnetization measurements

SIGRID G. EECKHOUT,1 EDDY DE GRAVE,1,* ANDRÉ LOUGEAR,2 MICHAEL GERDAN,2 CATHERINE A. MCCAMMON,3 ALFRED X. TRAUTWEIN,2 AND RENAUD VOCHTEN1

1Department of Subatomic and Radiation Physics, Ghent University, Belgium
2Institute for Physics, University of Lübeck, Germany
3Bayerisches Geoinstitut, University of Bayreuth, Germany

ABSTRACT

Magnetic properties of six Ca-free $P_2_1/c$ clinopyroxenes along the clinoenstatite-clinoferrosilite join were studied by transmission $^5$Fe Mössbauer spectroscopy (0.3–4.2 K) and SQUID magnetization measurements (2–300 K). The Fe$_{M_1}$,SiO$_3$ members were synthesized in a multi-anvil press, and samples with $x = 1.00, 0.91, 0.87, 0.78, 0.61,$ and 0.09 have been considered in this study. The magnetic order-disorder transition temperatures $T_N$ were determined by Mössbauer thermoscanning with zero source velocity. The magnetic Mössbauer spectra were refined using a full hyperfine-interaction Hamiltonian approach assuming different Fe$^{2+}$-Mg$^{2+}$ next-nearest-neighbor configurations of the probe nuclei to give a distinct spectral component. The different strengths of the M1 and M2 hyperfine fields can be related to the different 3D electronic level schemes as earlier determined from the paramagnetic Mössbauer spectra. The magnetic susceptibility measurements indicate a positive paramagnetic Curie temperature $\theta_p$ for FeSiO$_3$ ($x = 1$) above 50 K and a negative $\theta_p$ for $x \leq 0.91$ above 200 K. The Néel temperatures as determined from the susceptibility curves are equal to those obtained from the thermoscanning, indicating that spin relaxation effects can be ruled out. The macroscopic magnetic results further suggest ferromagnetic ordering of Fe$^{2+}$ ions within ribbons consisting of two linear bands of M2 sites that enclose chains of M1 sites, and antiferromagnetic coupling between neighboring ribbons. Generally spoken the magnetic behavior of Ca-free $P_2_1/c$ clinopyroxenes are similar to that of orthopyroxenes with similar (Mg,Fe) compositions.

INTRODUCTION

Ca-poor Mg-Fe pyroxenes are important components of the Earth’s crust and upper mantle. Depending on the external conditions of pressure and temperature they exhibit either an orthorhombic (opx) or a monoclinic (cpx) symmetry. The clinopyroxenes stable at ambient conditions are monoclinic with $P_2_1/c$ symmetry and transform to the high-density $C2/c$ phase under compression at room temperature (e.g., Angel et al. 1992; Hugh-Jones et al. 1994; Woodland and Angel 1997). The pyroxene structures consist of alternating SiO$_4$ tetrahedral chains and ribbons of sixfold coordinated octahedral bands, parallel to c. Mg$^{2+}$ and Fe$^{2+}$ occur at two non-equivalent oxygen octahedra, conventionally denoted as M1 and M2. Each ribbon includes a zigzag chain of M1 sites sandwiched between two linear bands of M2 sites. Recent information on the crystal structure of Ca-free $P_2_1/c$ pyroxenes has been provided by Angel et al. (1998).

Magnetic properties of Ca-poor Mg-Fe pyroxenes have only been published for the orthorhombic polymorphs, more specifically for the end-member ferrosilite (Ghose et al. 1988; Regnard et al. 1986; Regnard et al. 1987; Wiedenmann et al. 1986). It was suggested that a ferromagnetic coupling exists between the Fe species within a given ribbon formed by two M1 and M2 sites, however, some controversy remains concern-