Magnetic excitations and heat capacity of fayalite, Fe$_2$SiO$_4$

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INTRODUCTION

Magnetism in minerals is widespread and forms the basis of our knowledge of the past states of the geomagnetic field and plate tectonic motions and deformations of Earth’s crust. The foundations of rock magnetism are magnetic ordering and the magnetocrystalline anisotropy; the tendency of moments to align in certain “easy” crystallographic directions below the ordering temperature (O’Reilly 1984). One of the origins of this effect is spin-orbit coupling whereby the local moments respond not only to the mean magnetic field of the other moments or to external fields, but also to their bonding environment via the crystal field (Kittel 1976). The magnetocrystalline anisotropy generally depends strongly on temperature so that re-orientation of the moments is common. The most familiar example in rock magnetism is hematite, which transforms on cooling from a canted to a collinear antiferromagnet at the Morin temperature (265 K) (Morrish 1994). Like the order-disorder transition, canting influences the heat capacity and other thermodynamic properties.

Magnetic and electronic contributions to thermochemical properties can be large (Burns 1993; Wood 1981). The magnetic contribution to the entropy of fayalite is approximately 20% of the total entropy at room temperature (Robie et al. 1982a). The high temperature limiting value for magnetic plus electronic entropy arising from the t$_{2g}$ manifold of the Fe$^{3+}$ ions in an octahedral site is $R \ln 15 = 23 \text{ J/(mol·K)}$, larger than typical entropies of transition among the olivine polymorphs (Akaogi et al. 1989). Since the energy levels and associated thermodynamic contributions are sensitive to crystal structure, magnetic and electronic terms may significantly influence phase stability and element partitioning up to mantle temperatures. Electronic and magnetic excitations are also important for understanding electronic transitions, such as metal-insulator transitions (Williams et al. 1990), and as a probe of atomic scale physics, such as the structure of glasses (Kruger et al. 1992).

While electronic energy levels in minerals have been studied via optical spectroscopy (Burns 1993), comparatively little is known about magnetic energy levels, which are generally taken to be small modifications to the crystal-field levels via spin-orbit coupling. The nature of magnetic excitations can be complex, potentially involving spin waves in magnetically ordered states, spin glass behavior, frustration, critical scattering near the magnetic ordering temperature, and crystal-field excitations at all temperatures. For most minerals, including fayalite, there is no direct spectroscopic information available regarding the modifications to the crystal-field manifold due to magnetic effects; the energies of spin-orbit coupling, and exchange interactions are deduced via non-unique modeling of Mössbauer and magnetic measurements (Ballet et al. 1989; Ehrenberg and Fuess 1993; Fuess et al. 1988). Contributions to this problem from first principles theory are still limited: while spin-orbit coupling and non-collinear magnetism fall within the scope of modern density functional theory, these effects are ignored in recent studies of fayalite (Cococcioni et al. 2003; Jiang and Guo 2004; Wu et al.

ABSTRACT

We have used inelastic neutron-scattering measurements to study the magnetic excitations in the antiferromagnetic and paramagnetic phases of polycrystalline fayalite, Fe$_2$SiO$_4$. Sharp, nondispersing excitations are found in the ordered state, at 3.3, 5.4, 5.9, and 11.4 meV, and are interpreted as arising from the spin-orbit manifold of the Fe$^{3+}$ ions. These excitations are increasingly damped with increasing temperature, merging into a quasielastic continuum near the 65 K Neel temperature, although their energy does not vary with temperature. We have calculated the contribution of the heat capacity arising from these magnetic excitations and found that it compares favorably with the magnetic heat capacity deduced experimentally. Our analysis indicates that the M1 and M2 sites behave distinctly. The M1 site behaves quasi-locally and appears in the heat capacity as a Schottky anomaly that explains the shoulder in the heat capacity curve near 20 K, while the M2 site contributes predominantly to the critical lambda anomaly. The behavior of fayalite illuminates the nature of magnetic states in several related minerals, including others that also show shoulders and lambda anomalies in the heat capacity (tephroite), those that show only lambda anomalies (cobalt olivine and liebenbergite), and those that show only non-lambda anomalies (bronzite, anthophyllite, and almandine). We find no evidence to support the recent claim that some transition metal silicate and germanate olivines exhibit strong geometric frustration.

Keywords: Fayalite, neutron diffraction, calorimetry, phase transition, magnetic properties