An Analysis of the Magnetic Behavior of Olivine and Garnet Substitutional Solid Solutions

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The low-temperature magnetic and Néel temperature, T_N, properties of four silicate substitutional solid solutions containing paramagnetic ions are analyzed. The four systems are: fayalite-forsterite olivine, $Fe^{2+}_2SiO_4$-Mg_2SiO_4, and the garnet series, grossular-andradite, $Ca_3(Al_x,Fe^{3+}_{1-x})_2Si_3O_{12}$, grossular-spessartine, $(Ca_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$, and almandine-spessartine, $(Fe^{2+}_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$. Local magnetic behavior of the transition-metal-bearing end members is taken from published neutron diffraction results and theoretical calculations. T_N values are from calorimetric heat capacity, C_p, and magnetic susceptibility measurements. These end-members, along with more transition-metal-rich solid solutions, show a paramagnetic to antiferromagnetic phase transition. It is marked by a C_p λ-anomaly that decreases in temperature and magnitude with increasing substitution of the diamagnetic component. For olivines, T_N varies between 65 K and 18 K and T_N for the various garnets is less than 12 K.

Local magnetic behavior can involve one or more superexchange interactions mediated through oxygen atoms. T_N behavior shows a quasi-plateau-like effect for the systems fayalite-forsterite, grossular-andradite and grossular-spessartine. More transition-metal-rich crystals show a stronger T_N dependence compared to transition-metal-poor ones. The latter may possibly show superparamagnetic behavior. $(Fe^{2+}_x,Mn^{2+}_{1-x})_3Al_2Si_3O_{12}$ garnets show fundamentally different magnetic behavior. End-member almandine and spessartine have different and complex interacting local superexchange mechanisms and intermediate compositions show a double-exchange magnetic mechanism. For the latter, T_N values show negative deviations from linear interpolated T_N values between the end members. Double exchange occurs seldomly in oxides, and this may be the first documentation of this magnetic mechanism in a silicate.

T_N behavior may possibly be used to better understand the nature of macroscopic thermodynamic functions, C_p and $S°$, of both end-member and substitutional solid solutions phases.