American Mineralogist, Volume 100, pages 2231–2241, 2015

Trioctahedral Fe-rich micas: Relationships between magnetic behavior and crystal chemistry

Maria Franca Brigatti[1,*], Marco Affronte[2], Chiara Elmi[1], Daniele Malferrari[1] and Angela Laurora[1]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via G. Campi, 103, I-41125 Modena, Italy
[2]Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, Via G. Campi 213/a, I-41100 Modena, Italy

Abstract

Six Fe-bearing mica samples with different Fe ordering, $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio, octahedral, and tetrahedral composition were studied. Four micas belong to the phlogopite-annite join (space group *C*2/*m*), two are Mg-rich annite and two are Fe-rich phlogopite, one is a tetra-ferriphlogopite (space group *C*2/*m*) and one is Li-rich siderophyllite (space group *C*2). Thus these samples had a different environment around the Fe cations and layer symmetry. These micas were characterized by chemical analyses, single-crystal X-ray diffraction, X-ray absorption spectroscopy, and magnetic measurements. In samples with Fe mostly in octahedral coordination, dominant magnetic interactions among Fe atoms are ferromagnetic, which reach a maximum at higher $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios. Samples with higher $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio are also characterized by higher values of the Curie-Weiss θ constant. Where $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios decrease, θ values also decrease. The Fe^{3+}-rich phlogopite shows predominant Fe^{3+} in tetrahedral coordination and shows anti-ferromagnetic interactions with a negative value of the Curie-Weiss θ constant (i.e., θ = –25 K). Fe ordering in octahedral *trans*- and in one of the two *cis*-sites accounts for a greater θ value in Li-rich siderophyllite when compared to other samples showing similar octahedral Fe content. Our data suggest that Fe^{3+} cations and other non-ferromagnetic cations hinder long range magnetic ordering. This observation may produce for the different role of octahedral Fe magnetic interactions that can in principle develop along long Fe-rich octahedral chains, when compared to tetrahedral-octahedral interactions that are confined within the layer by the non-ferromagnetic cations of the interlayer. Spin glass behavior is indicated by the dependency of the temperature to produce maxima in the susceptibility curve. These maxima are related to the frequency of the applied AC magnetic field.

Keywords: Fe-rich micas, X-ray absorption spectroscopy, chemical analysis, single-crystal X-ray structure determination, magnetic measurements