Electronic structure of Fe-bearing lazulites

M. Grodzicki,[1,*] G.J. Redhammer,[1] G. Amthauer,[1] V. Schünemann,[2] A.X. Trautwein,[2] B. Velickov,[3] and P. Schmid-Beurmann[4]

[1]Institute of Mineralogy, University of Salzburg, Hellbrunner Str. 34, A-5020 Salzburg, Austria
[2]Institute of Physics, Medical University, Ratzeburger Allee 160, D-23536 Lübeck, Germany
[3]Institute of Applied Geosciences, TU-Berlin, Ernst-Reuter-Platz 1, D-10587 Berlin, Germany
[4]Institute of Mineralogy and Petrography, University of Kiel, Ludewig-Meyn-Str. 10, D-24098 Kiel, Germany

Abstract

The Fe end-members scorzalite [$Fe^{2+}Al_2^{3+}(PO_4)_2(OH)_2$] and barbosalite [$Fe^{2+}Fe_2^{3+}(PO_4)_2(OH)_2$] of the lazulite series have been investigated by Mössbauer and diffuse reflectance spectroscopy, and by electronic structure calculations in the local spin density approximation. The measured quadrupole splitting ($\Delta E_Q = -3.99$ mm/s) in scorzalite is in quantitative agreement with the calculated value ($\Delta E_Q = -3.90$ mm/s), as well as its temperature dependence. The optical spectrum of barbosalite can be resolved into three peaks at 8985 cm^{-1}, 10980 cm^{-1}, and 14110 cm^{-1}. These positions correlate well with the two calculated spin-allowed d-d transitions at 8824 cm^{-1} and 11477 cm^{-1}, and with an intervalence charge transfer transition at about 14200 cm^{-1}. The calculated low-temperature magnetic structure of barbosalite is characterized by a strong antiferromagnetic coupling ($J = -84.6$ cm^{-1}) within the octahedral Fe^{3+}-chains, whereas a weak antiferromagnetic coupling within the trioctahedral subunit cannot be considered as conclusive. The analysis of the charge and spin densities reveals that more than 90% of the covalent part of the iron-ligand bonds arises from the Fe(4s,4p)-electrons. Clusters of at least 95 atoms are required to reproduce the available experimental data with quantitative accuracy.