

## Mössbauer and optical absorption studies of aegirines

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Two chemically well analyzed natural aegirines were studied by Mössbauer and optical absorption spectroscopy. Aegirines belong to the clinopyroxenes and have the space group  $C2/c$ . The pure ferric is called compound is called acmite and has the chemical formula  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ . In the acmite structure Fe sites are occupies the sixfold coordinated M1 sites and  $\text{Na}^+$  fills the eightfold coordinated M2 sites. Acmite has the typical yellow-greenish colour originated by  $\text{Fe}^{3+}$  in silicates. In agreement with this, the optical absorption spectrum of one of our samples consists mainly of absorption bands due to  $\text{Fe}^{3+}$  in a slightly distorted octahedral ligand-field, probably intensified by  $\text{Fe}^{3+}$ - $\text{Fe}^{3+}$  interactions mainly in the  $\alpha$ -spectrum. The Mössbauer spectrum of the same acmite shows a ferric doublet, which is assigned to Fe at the M1 site.

In the second aegirine sample some  $\text{Fe}^{3+}$  is replaced by  $\text{Fe}^{2+}$  and the crystals are now dark-green and strongly pleochroic. The optical absorption spectrum of this sample reveals some  $\text{Fe}^{2+}$  absorption bands in addition to  $\text{Fe}^{3+}$  in the near infrared spectral region. The distinct pleochroism is mainly caused by a  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  intervalence charge transfer band at  $13330\text{ cm}^{-1}$ , which is strongly polarized in the  $\alpha$ -spectrum, e.g. almost parallel to the direction of the c-axis. The Mössbauer spectrum of the second sample exhibits, in addition to an  $\text{Fe}^{3+}$  doublet, an  $\text{Fe}^{2+}$  doublet both assigned to M1. There is another broad intermediate absorption pattern of which relative area increases on raising temperature in the Mössbauer spectrum, which represents some  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions involved in a thermally activated electron delocalization process. The present study suggests that electron delocalization in aegirines occurs preferentially within the infinite chains formed by edge-sharing M1 octahedra parallel to the c-axis.