

THE INFLUENCE OF ION-PAIR INTERACTIONS ON SITE OCCUPANCY DETERMINATIONS

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Metal ions in neighboring crystallographic sites interact in several ways to influence properties such as color and pleochroism and, in turn, quantitative determinations of site occupancy by optical and Mössbauer spectroscopy. Interactions between iron ions and iron and titanium ions are often observed in silicate minerals. They are particularly prominent in dravites of red-brown color from Kenya and Brazil. Mössbauer spectra of the Kenyan dravite are characterized solely by ferric iron and show an anomalously low intensity. This anomaly reflects a phenomenon which may lead to underestimates of the concentration of iron as determined by Mössbauer spectroscopy. The optical spectra are dominated by Fe^{2+} features. Fe^{3+} is evident in the spectra only by its uv metal-oxygen charge transfer edge and a crystal field transition of Fe^{3+} of unusually high intensity. This intensification arises from magnetic interactions between Fe^{3+} ions. Although red color in tourmalines is commonly due to a high Mn content, in this case, interaction between iron and titanium (evident in an intense $\text{Fe}^{2+}/\text{Ti}^{4+}$ intervalence charge transfer transition at 485 nm) is the principal cause of this color. Transitions at 800 and 1100 nm which are usually associated with noninteracting Fe^{2+} ions show unusual intensity increases at low temperature. This behavior, observed in corundum and biotite (Smith, 1978) and commonly in tourmaline, reflects an interaction of Fe^{2+} with Fe^{3+} ions. The greater intensity of these transitions in tourmaline is also the result of ion-pair interactions as evidenced by low iron elbaïtes which show neither intensity increases nor polarization differences. The demonstrated effect of ion-pair interactions on the intensity of spectroscopic data point to their necessary consideration in quantitative spectroscopic measurements of site occupancy.