ANOMALOUS FERROUS IRON OPTICAL ABSORPTION INTENSITIES IN TOURMALINE

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Much of the pleochroism and intense coloration of minerals has been recognized as arising from intervalence charge transfer occurring by interaction among groups of transition metal ions of differing oxidation states (IVCT). We have observed equally intense absorption associated with a different effect of this interaction involving the intensification of Fe^{2+} transitions. This behavior is particularly evident in iron-rich tourmalines in which Fe^{2+} transitions are increased by as much as a factor of ~50. Intensification of Fe^{2+} absorption bands is the dominant factor governing the pleochroism of tourmaline and has undoubtedly been an unrecognized factor in other minerals. This effect can thus produce large errors in site occupancies and Fe^{2+}/Fe^{3+} ratios determined by optical absorption intensities of Fe^{2+} transitions. This effect appears to be related to interaction between Fe^{2+} and Fe^{3+} as was proposed by Smith (1978).

The optical behavior of the tourmaline group provides a delineation of the magnitude and characteristics of this interaction. At low iron contents, absorption in both polarizations is of non-interacting Fe^{2+}, yielding absorbance ratios $E \perp c / E \parallel c$ of ~1. As the iron content increases the ratio of $E \perp c / E \parallel c$ increases and the temperature response for $E \perp c$ no longer represent absorption by isolated Fe^{2+} ions. The highest $E \perp c / E \parallel c$ ratio is observed in a ferric-rich schorl which yields an approximate molar absorptivity of ~200 l/mol/cm based on Fe^{2+} content. Isolated Fe^{2+} ions in tourmaline should have molar absorptivities ≤ 10. Fe^{2+}/Fe^{3+} interaction is also reflected by increases in integrated intensity at 77 K. This effect can occur in the absence of strong IVCT, and unlike IVCT which produces a new feature, it acts upon absorption features present in the absence of ion-pair interactions.