INTENSIFIED Fe^{2+} d-d BANDS IN MIXED VALENCE SOLIDS. Stephanie M. Mattson and George R. Rossman, Div. of Geological & Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

The interaction of heterovalent transition metal ions often produces well-recognized optical absorption due to intervalence charge transfer (IVCT). Equally intense absorption is produced by intensified d-d bands, a different effect of this interaction. We have observed increases up to a factor of ~50 for Fe^{2+} from the interaction of Fe^{3+} with Fe^{2+} in iron-rich tourmalines. Absorption is intensified along the metal-metal vector and increases at low temperatures. Integrated intensity may increase two-fold at 77 K vs 295 K. Both components of the $^5T_{2g} \rightarrow {}^5E_g$ band are intensified. The direction of the metal-metal vector for edge-shared transition metal sites in the mineral tourmaline is perpendicular to the c-axis and it is in this direction that the intensification is observed. At low Fe contents, absorption both in E⊥c and E∥c is of non-interacting Fe^{2+} with ε ~1 to 5 and polarization ratios of ~1. Above 3 mol/l of Fe minimum ε's based on total iron content range from 50 to 100 in E⊥c and remain <7 in E∥c. Fe^{2+} ε's for sites of the size and symmetry available in tourmaline are generally <10. The influence of Fe^{3+} is demonstrated by an increase in the E⊥c/E∥c ratio from 13 to 21 in a sample whose Fe^{3+}/Fe^{2+} ratio was increased through oxidation. The Fe^{2+} intensity in the unintensified direction (E∥c) decreased by ~20%, reflecting the true loss of Fe^{2+}. Likewise, an unusually Fe^{3+}-rich natural sample exhibited the highest E⊥c/E⊥c ratio of ~50 and had an ε of 200 in E⊥c based on Fe^{2+} content. Unlike IVCT, this effect does not produce a new transition and thus has probably gone unrecognized in other systems.