

Why Hematite is Red

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The spectroscopic properties of interacting pairs or clusters of transition metal ions are relatively less well understood than those of isolated ions. Particularly important are the interactions between ions such as Fe^{3+} which have optical absorption dominated by spin-forbidden processes. Normally pale colored when isolated from each other, Fe^{3+} ions produce intense colors when interacting with each other. Andradite garnet is a pale colored mineral with a high concentration of isolated Fe^{3+} and hematite is an example of a mineral which owes its intense color to interactions among Fe^{3+} ions.

To better quantify these phenomena, the optical absorption intensities and magnetic susceptibilities of a series of minerals was examined. A general correlation was established between the intensity of the absorption bands derived from the ${}^4\text{T}_{1g}$ and (${}^4\text{A}_{1g}$, ${}^4\text{E}_g$) states and the extent of the magnetic coupling between the ions. Decreased magnetic susceptibilities are associated with strong magnetic interactions which in turn are associated with high optical band intensities.

For Fe^{3+} the intensities of distorted sites are greater than those of regular sites, but the effects of distortion are small compared to the band intensification caused by magnetic interaction.

The ϵ -values for the (${}^4\text{A}_{1g}$, ${}^4\text{E}_g$) bands of minerals with isolated Fe^{3+} are on the order of 1 and those with isolated, distorted sites can be about 5 whereas those with chains and clusters of Fe^{3+} with oxide coordination range from 30 to nearly 100.