

## Conference on Charge Transfer

Reported by H.S. Waff.

The afternoon session opened with a discussion of magnetic ordering, clustering of iron, and manifestations in optical spectroscopy by G.R. Rossman (Cal Tech ). Isolated Fe in solution, iron phosphate, and andradite garnet are all cases in which Fe<sup>3+</sup> has no next-nearest-neighbor interaction with another Fe<sup>3+</sup> ion. Even though these three represent nonequivalent types of Fe<sup>3+</sup>, they are spectroscopically very similar. If more than one Fe<sup>3+</sup> ion is brought into next-nearest-neighbor position, magnetic ordering (super exchange) can occur. In the case of two ferric ions in octahedral ligation and linearly bridged by an oxygen ion (dimeric iron) there is an increase in intensity of the first and second ligand field bands by 2 orders of magnitude. This increase is accompanied by an increase of magnetic moment. The OH-bridged irons also interact magnetically, producing some optical enhancement but not nearly as much as is obtained with oxygen-bridged dimeric iron. However, Rossman reported that the presence of hydroxyl ions in the crystal lattice, even in minor concentrations, causes a pronounced shifting of the charge transfer bands toward the visible; more pronounced shifts toward the visible are obtained with increasing magnetic interaction. Oxy-bridged orderings are basically short-range phenomena and therefore apply just as well in amorphous and crystalline materials. In addition, structural detail is added by strong magnetic coupling, and the apparent ultraviolet edge is moved down, dominating sample color.

The recurrent theme of polarization of the charge transfer bands again entered clearly in Rossman's examples. These bands are polarized with E vectors along the metal-metal axis with intense absorption. The E vectors perpendicular to this axis produce no charge transfer absorption and result in nearly colorless transmitted light.