

- McCLURE, D. S. (1959) Electronic Spectra of Molecules and Ions in Crystals. II Spectra of Ions in Crystals, In *Solid State Physics*. Academic Press, New York, p. 9.
- WHITE, W. B. AND K. L. KEESTER (1966) Optical absorption spectra of iron in the rock forming silicates. *Amer. Mineral.* **51**, 774-790.

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OPTICAL ABSORPTION SPECTRA OF IRON IN THE ROCK-FORMING
SILICATES: REPLY

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In the treatment of the spectra of iron in the common silicates (White and Keester, 1966) only the crystal (or ligand) field theory was invoked because this theory is not only quite adequate to explain all spectral *bands* observed in the spectral region measured but because this theory permits fairly straightforward interpretation with a minimum of assumption and calculation. We did not, in a short introduction to a mainly experimental paper, make the presumption of presenting the mineralogical community with a lecture on solid state physics. I am quite sorry that the critic chose to interpret our remarks as a sweeping exclusion of all other electronic processes from the spectra of minerals simply because these were not discussed. However, since the matter has been brought up and because there is apparently some confusion on the origin of color in minerals a few comments on alternative electronic processes may be appropriate.

I do not find the "charge transfer spectrum" concept of very great value. This term is used as a catch-all for a wide variety of electronic processes which give rise to strong absorption in the visible and ultraviolet and there is a great danger in merely assigning any unexplained feature in the spectrum as a "charge transfer band." Secondly, the concept was developed for molecular complexes and is of questionable value when applied to a periodic lattice in which various de-localizations of electrons can also take place.

The spectra of the iron silicates do exhibit, as the critic notes, a strong absorption at the ultraviolet end of the spectrum and it seems reasonable to suppose that this is the low frequency tail of some intense but unobserved band lying at higher frequencies. Since the band was not observed, we would hardly have been justified in proposing an interpretation or even hanging a "charge transfer" label on the low frequency tail.

The critic points to the example of the permanganate ion as an example of a highly colored transition metal compound whose spectrum must be treated by molecular orbital theory and he is quite right. In MnO_4^- , CrO_4^{2-} and in many other anions formed around metal ions with a high formal charge there are well-developed covalent bonds and one observes in the spectra transitions between molecular orbital states. These spectra are usually quite intense but are not "charge transfer" spectra in the same sense that other transitions discussed below are "charge transfer" spectra. Such spectra would be of importance in discussing the colors of crocoite and perhaps the vanadate, molybdate, and tungstate minerals.

The molecular orbital theory, particularly as it applies to bonds involving the d -electrons or the empty d -orbitals (as in the case of the d^0 ion) can be treated as an extension of the ligand field theory and the same group theoretical arguments can be used for constructing proper molecular orbitals from mixtures of metal and anion atomic orbitals. There is indeed a continuous series of spectral types ranging from those of purely ionic crystals for which even the electrostatic approximations of the crystal field theory hold pretty well to those of a completely covalent molecule of which the MnO_4^- ion and the chromate ion are good examples. Fe^{3+} was cited as an example of an ion in which "charge transfer" bands may completely obscure the weaker $d-d$ spectra. And yet this is not necessarily correct. We called particular attention to the spectrum of chlorite as an example of a structure in which Fe^{3+} exhibited a crystal field spectrum unobscured by Fe^{3+} - Fe^{3+} interactions. The more usual brown color observed in hematite, goethite, biotite and many other iron minerals might be thought to indicate the situation the critic describes. In contrast we have very recently obtained spectra on thin single crystals of hematite and biotite and find that the same set of absorption bands is present that occurs in chlorite. The intensities are higher and the frequencies are shifted somewhat but the conclusion must be that the deviation from a "crystal field" type spectrum toward a "charge transfer" spectrum is not great in these minerals in spite of the dramatic change in color.

Transitions between a tightly bound one-nucleus ground state (a "crystal field" level) and a bound multi-nucleus molecular orbital-like excited state probably occur in the high-energy portions of most mineral spectra. They are difficult to characterize and distinguish from other highly energetic transitions in the solid but would be examples of true molecular-like charge-transfer spectra.

Other charge-transfer phenomena occur in crystals (but not in molecules in solution or in vapor) of which the most important is the fundamental absorption edge. The absorption edge in an insulating solid

marks a transition from a bound state in the lattice to a de-localized state in which the electron becomes free to move. This spectral feature is 10^4 to 10^6 times as intense as the *d-d* transitions and marks the practical low wavelength limit of the spectra. In silicates, this transition is in the ultraviolet and the crystals are usually transparent to visible and near-infrared radiation when only filled-shell cations are involved. In sulfides, arsenides and related minerals, the absorption edge may be at much lower energies. Thus cinnabar owes its bright red color to fact that the absorption edge is in the visible and only the low-frequency red light is transmitted. Other minerals such as galena owe their metallic luster to an absorption edge in the infrared so that the reflectivity of visible light from galena is metallic. The absorption edge represents a transition from the valence to the conduction band of the crystal and thus the band theory of solids (Nussbaum, 1966) (much more difficult mathematically than the crystal field theory) is the appropriate model on which to discuss the deep colors of most sulfide minerals including the transition metal sulfides.

In some crystals containing transition metals in shared-edge or shared-face oxygen coordination polyhedra the possibility exists of direct overlap of the *d*-orbitals to form narrow conduction bands. Narrow bands can also form through overlap of the *d*-orbitals through the oxygen *p*-orbitals (Goodenough, 1963, 1965). Transition between these narrow bands are dipole-allowed and give rise to very intense spectra in certain corundum- and rutile-structure oxides such as V_2O_3 , VO_2 , TiO_{2-x} etc. (Porter, White, and Roy, 1966). Work now underway indicates that the spectra of the Ti^{3+} -containing blue kyanites and star sapphires may have to be treated by this model. In the limit as the overlap goes to zero this band model blends into a crystal field model.

Still another type of "charge transfer" process may occur when ions of different valence are present on the same lattice site, as in the case of Fe^{2+} and Fe^{3+} in magnetite. Fe^{2+} and Fe^{3+} can exchange an electron by an electron-hopping process, giving rise to semi-conduction and also to broad absorption features in the optical spectrum. The color of magnetite and certain other spinels is due at least in part to this process.

Exciton theory was invented to explain certain fine structure which appears in the spectra of alkali halides and some semiconductors just below the absorption edge. The semi-conductor exciton is a mobile electron-hole pair bound together by mutual interaction. Both observation and theory are quite well developed (Moss, 1961; Schulman and Compton 1963; Knox, 1961) but whether this theory will prove useful when applied to the more complex mineral structures is not yet known.

The object of this discussion has been to answer the critics' contention

that we made the dogmatic assumption that the crystal field model will explain all mineral spectra by outlining some of the wide variety of electronic processes which give rise to color in minerals. The application of these processes to the spectra of various classes of minerals and, more particularly, the use of the results to the interpretation of structural detail, and to mineral paragenesis, will remain a rich field for research.

REFERENCES

- GOODENOUGH, J. B. (1963) *Magnetism and the Chemical Bond*. John Wiley and Sons, New York.
- (1965) Transition-metal oxides with metallic conductivity. *Bull. Soc. Chim. France*, 1200–1207.
- KNOX, R. S. (1963) Theory of Exciton. *Solid State Phys.*, Suppl. 5.
- MOSS, T. S. (1961) *Optical Properties of Semi-Conductors*. Butterworths and Co. Ltd., London.
- NUSSBAUM, A. (1965) Crystal symmetry, group theory, and band structure calculations. *Solid State Phys.* 18, 165–272.
- SCHULMAN, J. H. AND W. D. COMPTON (1963) *Color centers in solids*. Pergamon Press, New York.
- PORTER, V. R., W. B. WHITE AND R. ROY (1966) Optical spectra of semi-conducting transition metal oxides. *Bull. Amer. Ceram. Soc.* 45, 810.
- WHITE, W. B., AND K. L. KEESTER (1966) Optical absorption spectra of iron in the rock-forming silicates. *Amer. Mineral.* 51, 774–791.