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

W. H. Turner, *Owens-Illinois Technical Center, Toledo, Ohio.*

I must raise a strenuous objection to many of the explicit statements and implicit assumptions made by W. B. White and K. L. Keester in their paper "Optical Absorption Spectra of Iron in the Rock Forming Silicates" (1966). Ligand field theory, which is used to explain their data, is a practical and elegant model, but is clearly limited to certain types of spectra. One must not make premature and dogmatic assumptions that any one of several possible models will uniquely explain all the data which will be obtained. Alternative models are often necessary such as molecular orbital theory, exciton theory, and band theory.

For example, White and Keester state "the characteristic colors of transition metal ions in aqueous solution and crystals are due to electronic transitions within the unfilled *d*-orbitals of the ions," and that "the theoretical explanation for these effects in terms of the crystal or ligand field theory (Ballhausen 1962; McClure 1959) is now well established and can be directly applied to the explanation of the iron mineral spectra."

Except for the qualifier "characteristic colors," this statement rules out the possibility of charge transfer spectra which usually must be treated by molecular orbital theory rather than ligand field theory. Even this qualification does not limit the applicability of ligand field theory sufficiently to make such statements even generally true. The characteristic color of the permanganate species has been explained only by molecular orbital theory. Note that Mn^{7+} has a d^0 configuration, thus, no *d-d* transitions.

In most cases, iron provides another example of spectra not due to *d-d* transitions, having strong charge transfer bands in addition to the much weaker *d-d* spectra. In the ferric ion the former may completely obscure the latter (Cotton and Wilkinson, 1962).

Although White and Keester cite McClure for theoretical justification for their ligand field model, I suggest they review his penetrating discussion of the limitations and areas of applicability of ligand field theory, molecular orbital theory, and exciton and/or band theory. As McClure ((1959), Part II, Section II. 5) states, "the term charge transfer spectrum could be applied with some justification to many observed spectra. . . . Either the initial or final state is localized mainly on the atoms surrounding a central metal ion."

These charge transfer spectra may often be treated by a molecular orbital model, and do not require unfilled *d*-orbitals to be present. It should be emphasized that molecular orbital theory will not correctly treat all charge transfer bands. In principle, it should only be used when discrete complexes or molecular species are involved. When speaking of the more ionic solids, McClure (1959, Part II, Section I, 2 (e)) notes: "Charge transfer in the latter (case) contributes to the formation of an exciton or conduction band. The band width becomes an important feature of the spectrum as the ionic crystal limit is approached and band theory must be applied to calculate it."

Based on the above considerations, the *a priori* assumption of a ligand field model for all features of the iron mineral spectrum seems highly questionable. Indeed, all the spectra show a strong absorption at the high energy end of the visible which—as the authors correctly state—is due to an intense UV absorption which extends into the visible. This provides a characteristic green color instead of the blue which would be seen if the one micron (10^{+4} cm^{-1}) ferrous absorption were the only band present. Other workers have assigned this UV band to a charge transfer band (Bates, 1962).

Since the authors recognize the presence of this band, yet fail to assign it to a ligand field transition, they have placed themselves in the unfortunate predicament of having their statements and assumptions contradicted by their own experimental evidence.

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

William B. White, *Materials Research Laboratory and Department of Geochemistry and Mineralogy, Pennsylvania State University, University Park, Pennsylvania.*

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.