Polarization-dependence and Oscillator Strengths of Metal–Metal Charge-transfer Bands in Iron(II,III) Silicate Minerals

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SILICATE MINERALS which contain both ferrous and ferric iron commonly have an absorption band in the red (6200—7400 Å) which is absent when either ion is present alone, suggesting assignment to $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer. Examples[1] include tourmaline, trioctahedral micas, alkali amphiboles,[2] cordierite,[3] and kyanite.[4] We have now found that the integrated intensity of the 7200 Å band in fifteen analysed micas containing 0·3 to 25% FeO and 0·3 to 6% Fe_2O_3 is proportional to the product of the mole fractions of ferrous and ferric iron; this confirms the assignment, and enables us to determine the oscillator strength and polarization dependence of this transition for the first time. A knowledge of such charge-transfer processes is important in understanding the electronic and magnetic properties of transition-metal compounds, their reaction mechanisms and kinetics.

Absorption spectra of mica and tourmaline were measured on oriented thin sections or cleavage flakes mounted in the sample beam of a Cary 14H spectrophotometer, using a Nicol prism as polarizer. The spectra were digitized, and partially overlapping bands were resolved by an iterative least-squares procedure, assuming a Gaussian band shape.

In all the minerals cited in Table 1, the ratio of the absorbances measured along the three principal vibration directions (x, y, z) is close to the ratio of the squares of the direction cosines of the donor $\rightarrow$ acceptor vector calculated from the atomic

TABLE 1

Charge-transfer bands in some silicate minerals

Structure	Symmetry	$\bar{\nu}$(kK)	$w_{\frac{1}{2}}$(kK)	$[c]$	n	$\alpha_{\parallel}$	$f_{\parallel}$	$\epsilon_{\parallel}$	Fe–Fe distance	Polarization dependence
Tourmaline ..	$R3m$	13·8	3·4	0·028	6	1200	0·018	975	3·04 Å	$y = z,\ x = 0$
Biotite mica[a] ..	$C2/m$	13·7	3·3	0·004	32	256	0·005	280	3·1	$z > y,\ x = 0$
Chlorite ..	$C2/m$	14·5	3·0	—	32	48	—	—	3·1	$z > y,\ z = 0$
Cordierite ..	$Cccm$	17·0[b]	3	0·003	4	20	0·003	340	⩾2·85	$z > y,\ x = 0$
Kyanite ..	$P\bar{1}$	16·7[c]	3	⩽0·0003	2	5	⩾0·005	⩾150	⩾2·79	$z > y > x$
Glaucophane ..	$C2/m$	16·1[d]	3	—	—	—	—	—	3·1, 3·25	$a^* = 0,\ b,\ c$ finite

[a] This sample contains 7·71% FeO and 1·84% Fe_2O_3. Fourteen other micas gave similar results. [b] Assigned to a $t_{2g} \rightarrow e_g$ transition in Fe^{2+} by Farrell and Newnham (ref. 3) and reassigned by us (ref. 1). [c] Assigned to an unspecified transition of Ti^{3+} by White and White (ref. 4) and reassigned by us (ref. 1). [d] Reflectance spectrum, referred to crystallographic axes.

TABLE 2

Homonuclear spin-allowed optical transitions in d^n *systems* (*octahedral*)

Mechanism		Donor		Acceptor	Examples
t_{2g}–t_{2g} and t_{2g}–$p(\pi)$–t_{2g}	$n(t_{2g})$	1,2,3	→	0,1,2	$Ti^{3+} \rightarrow Ti^{4+}$
		4,5,6	→	3,4,5	$Fe^{2+} \rightarrow Fe^{3+}$
e_g–$p(\sigma)$–e_g	$n(e_g)$	1,2	→	0,1	$Ni^{2+} \rightarrow Ni^{3+}$, $Pt^{2+} \rightarrow Pt^{3+}$
		3,4	→	2,3	$Au^{+} \rightarrow Au^{3+}$, $Cu^{+} \rightarrow Cu^{2+}$

co-ordinates, implying that the transition moment is directed rather accurately along this vector. In other words, the transition is excited only by that component ($E_{\parallel}$) of the electric vector of light which lies along the donor → acceptor vector. The corresponding absorption coefficient $\alpha_{\parallel}$ is equal to $\alpha_x + \alpha_y + \alpha_z$, or simply to 3α in a cubic crystal or other isotropic medium. We have defined[1] the oscillator strengths ($f_{\parallel}$) and extinction coefficients ($\epsilon_{\parallel}$) using:

$$f_{\parallel} = 2{\cdot}35 \times 10^{-12}\, \alpha_{\parallel} V w_{\frac{1}{2}}/n[c] \text{ per ion-pair per second}$$

$$\epsilon_{\parallel} = 4{\cdot}35 \times 10^{-4}\, \alpha_{\parallel} V/n[c] \text{ litres mole}^{-1}\text{ cm.}^{-1}$$

where V is the molar volume, n is the number of nearest neighbour donor → acceptor contacts per formula unit, $[c]$ is the product of the mole fractions of donor and acceptor ions, and $w_{\frac{1}{2}}$ is the band width at half height in wavenumbers. Typically $0{\cdot}005 < f_{\parallel} < 0{\cdot}02$ and $200 < \epsilon_{\parallel} < 1000$, compared with values of $f \sim 10^{-5}$ and $\epsilon \sim 10$ for spin- and symmetry-allowed *d–d* transitions of ferrous iron, and $f \sim 0{\cdot}2$, $\epsilon \sim 2500$ for the broad $O^{2-} \rightarrow Fe^{2+}$ charge-transfer band in micas.[1]

Of the three types of overlap which are thought to influence magnetic order and electronic conduction in transition-metal oxides,[5] only the direct exchange (t_{2g}–t_{2g}) and indirect (t_{2g}–$p(\pi)$–t_{2g}) superexchange mechanisms give rise to allowed optical transitions in high-spin iron compounds (Table 2). Since it is improbable that t_{2g}–t_{2g} overlap between iron atoms 3·0 to 3·3 Å apart would give oscillator strengths as high as 0·02, the t_{2g}–$p(\pi)$–t_{2g} mechanism is preferred to direct exchange. This may be compared with the situation in the gold(I,III) and platinum(II,IV) charge-transfer complexes studied by Yamada and Tsuchida,[6] in which only the e_g–$p(\sigma)$–e_g mechanism can operate (Table 2). Direct exchange is permitted, and may well occur, in Ti_2O_3 and V_2O_3.[5]

Studies[2,7] of electronic conduction in iron(II,III) silicates indicate that phonon-assisted charge-transfer has an activation energy of 0·6 to 0·8 ev, compared with our values of 1·7 to 2·1 ev for optical excitation. Similar differences (0·8 and 2·1 ev) were found in chlorocuprate(I,II) complexes,[8] and reflect the much larger departure from the equilibrium metal–ligand distances in the optical transition complexes.

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