

Charge-transfer in ferromagnesian silicates: The polarized electronic spectra of trioctahedral micas

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SUMMARY. Polarized spectra (2000 to 25 000 Å) have been obtained for fifteen analysed trioctahedral micas covering a wide range of compositions, and including four phlogopites, nine biotites, and two lepidomelanes. Three main contributions to the absorption have been noted: charge transfer from oxygen to ferrous iron throughout the visible and near ultraviolet, charge transfer from ferrous to ferric ions at the red end of the visible spectrum and internal *d-d* transitions of ferrous ions in the near infrared.

Substitutions in the brucite layer (especially Ti) cause the $O \rightarrow Fe^{2+}$ band to broaden, and thus to encroach on the visible region for vibration directions in the plane of the cleavage flake. The transmission window between these bands is further blocked by the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band, which is polarized in the plane of the flake. The overall effect is to produce very strong absorption throughout the visible region for (β , γ) vibration directions, and relatively weak absorption for α , i.e. the observed very strong pleochroism of biotite.

Many features of the spectra of chlorite, amphiboles, and tourmaline, which contain octahedral ions in brucite-like sheets, strips, and fragments respectively, may be interpreted by analogy with biotite.

Two types of solid solution effect are described: substitutional broadening, which is responsible for the extension of the $O \rightarrow Fe^{2+}$ band into the visible region in biotites and aluminous orthopyroxenes, and substitutional intensification, which permits in solid solutions transitions that are forbidden by the conventional selection rules.

THE strong colour and spectacular pleochroism of biotite micas has long attracted attention, and a number of attempts have been made to correlate colour with composition. Weyl (1951) and some later workers attributed the strong absorption of light vibrating in the plane of the cleavage flake to charge-transfer from Fe^{2+} to Fe^{3+} . Hayama (1959) noted that micas with high FeO and Fe_2O_3 contents were green, whilst addition of TiO_2 caused them to become reddish-brown. Robbins (1967) reported on the spectra of 15 trioctahedral micas and a number of related minerals, and assigned the three prominent absorption bands in the visible and near infrared to metal-metal charge-transfer and internal *d-d* transitions of ferrous iron, confirming the assignments by demonstrating graphically the proportionality between band

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and thickness, after correction for reflection losses using the Fresnel formula for normal incidence: $R = (n-1)^2/(n+1)^2 \simeq 5\%$ for $n = 1.6$; $D = \log_{10}(I_0 - R)/I_t$.

Band parameters, viz. width at half height ($w_{1/2}$), linear absorption coefficient to base e at maximum absorption (α_0) and wavenumber of maximum absorption (ν_0), were obtained by digitizing the spectra at intervals of 250 cm^{-1} or less, and resolving overlapping bands by an iterative least-squares procedure, assuming Gaussian band shapes. The integrated intensity of the band (A) and its oscillator strength (f) are given by: $A = \alpha_0 \cdot w_{1/2} \sqrt{\pi/2}$ and $f = 1.877 \times 10^{-12} AV/n$, where V is the molar volume in cm^3

TABLE I. *Partial analyses and γ indices of trioctahedral micas*

	P2	P3	P4	P1	B6	B1	B5	B10	B8
FeO	0.37	1.19	1.82	2.71	3.00	7.46	7.71	7.93	11.72
Fe ₂ O ₃	0.34	0.82	3.97	0.96	0.78	3.01	1.84	3.14	4.86
TiO ₂	0.23	0.85	0.93	0.70	2.53	3.54	1.36	5.92	3.37
γ	1.557	1.603	1.601	1.592	1.598	1.596	1.603	1.622	1.628
Fe ³⁺	0.05	0.13	0.22	0.32	0.36	0.90	0.94	0.96	1.47
Fe ³⁺	0.04	0.09	0.47	0.11	0.09	0.35	0.16	0.37	0.57
Ti ⁴⁺	0.02	0.09	0.10	0.08	0.28	0.40	0.15	0.66	0.38
	B7	B2	B9	B3	L1	L2	HM5	HM6	
FeO	12.21	14.41	17.11	17.64	17.74	24.75	3.21	16.35	
Fe ₂ O ₃	2.83	4.12	5.46	4.88	4.43	5.02	0.32	4.75	
TiO ₂	2.78	2.84	2.78	4.14	2.97	4.82	2.22	3.36	
γ	1.632	1.615	1.660	1.652	1.655	1.676	—	—	
Fe ²⁺	1.54	1.84	2.22	2.27	2.29	3.30	0.37	2.20	
Fe ³⁺	0.33	0.48	0.64	0.58	0.53	0.59	0.03	0.58	
Ti ⁴⁺	0.31	0.32	0.31	0.46	0.33	0.54	0.24	0.40	

Prefixes P, B, and L refer to minerals described as phlogopites, biotites, and lepidomelanes in the collection of the Department of Earth Sciences, University of Leeds. These names have been retained. Localities and parageneses (where known) are given by Robbins (1967). The analyses have been recalculated graphically to 22(O, OH, F). HM 5 and 6 refer to Hogg and Meads (1970).

and n is the number of absorbing atoms per formula unit. Another quantity often used by chemists is the extinction coefficient defined by: $\epsilon_0 = D_{\max} V/1000 n$. Use of the extinction coefficient can be misleading, since it is often difficult to define n , e.g. when the absorbing ion is present in several crystallographically non-equivalent sites, only one of which contributes intensity to any one band. Also, two bands having identical integrated intensities but differing in width have different values of ϵ .

Partial analyses of the samples are given in table I. Total iron was determined by the α : α' -dipyridyl method, FeO by Wilson's (1960) vanadate method, and TiO₂ by X-ray fluorescence.

Structure and composition of trioctahedral micas

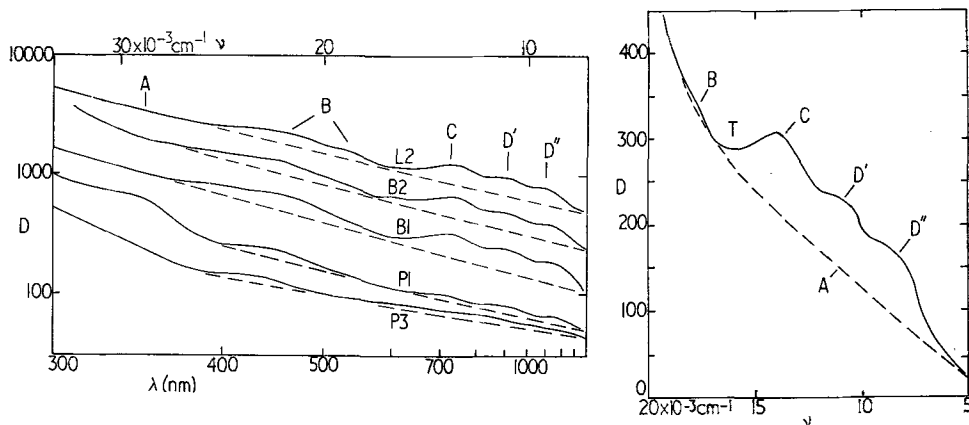
In common with other micas, the structure of minerals of the phlogopite-biotite series is based on a composite sheet consisting of a brucite-like layer of octahedrally coordinated cations sandwiched between two silicate layers of nominal composition $(\text{Si}_3\text{AlO}_{10})_n$. These composite sheets are bonded to their neighbours by interlayer potassium ions. Natural biotites are basically trioctahedral micas, with some dioctahedral character which is indicated by the presence of octahedral vacancies (\square) in the formula unit: $\text{K}(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}, \text{Ti}, \square)_3(\text{Si}_{4-n}\text{Al}_n\text{O}_{10})(\text{OH})_2$, where $0.9 < n < 1.5$. In space group $C2/m$, one of the three octahedral ions in the formula unit (designated c) occupies a site of symmetry $2/m$, whilst the other two occupy sites (designated h) of symmetry 2. In dioctahedral micas the two h positions are occupied by trivalent ions, c being vacant (Veitch and Radoslovich, 1963). Considerations of ionic radius and charge balance suggest that in biotite small ions of charge > 2 will prefer h sites, whilst vacancies and larger bivalent ions will prefer the c position. This deduction has been confirmed by infrared (Vedder, 1964) and Mössbauer spectra (Hogg and Meads, 1970). The chemical and structural complexity of the trioctahedral micas is such that it is impossible to deduce cation distributions unequivocally, but using the Mössbauer data of Hogg and Meads and the principles outlined above we calculate for an Indian phlogopite, HM5 (comparable to P1 and B6) $\text{Fe}_{0.07}^{2+}\text{Mg}_{0.88}\square_{0.55}$ in c and $2(\text{Fe}_{0.06}^{2+}\text{Fe}_{0.01}^{3+}\text{Mg}_{0.84}\text{Al}_{0.04}\text{Ti}_{0.06})$ in h , and for the Aberdeen biotite HM6 (comparable with B9, B3, and L1) $\text{Fe}_{0.60}^{2+}\text{Mg}_{0.18}\square_{0.22}$ in c and $2(\text{Fe}_{0.24}^{2+}\text{Fe}_{0.12}^{3+}\text{Mg}_{0.46}\text{Al}_{0.10}\text{Ti}_{0.10})$ in h .

Interpretation of the spectra

The ω -spectra of representative phlogopites, biotites, and lepidomelanes containing from 1.2 to 24.8 % FeO and varying amounts of TiO_2 and Fe_2O_3 are shown in fig. 1. By making use of the Urbach relation (Urbach, 1953; Davydov, 1968), and plotting $\log D$ against wavenumber, rather than D against ν or λ as is customary, the tail of the underlying (intrinsic) absorption band (A) is rendered nearly linear, and the much narrower $d-d$ and metal-metal charge-transfer bands are clearly displayed. Four such bands or band systems occur at 4000 to 6000 Å (B), 7200 (C), 9200 (D'), and 11 500 Å (D'') and these are shown in more detail in fig. 2.

Intrinsic absorption

Assignment: The intensity of the underlying band (A) is clearly related to the FeO content (fig. 1), and a plot of absorption against FeO content is linear (fig. 3). Attempts at curve fitting suggest $\alpha_0 \simeq 37\,000\text{ cm}^{-1}$, $w_{\frac{1}{2}} \simeq 4300\text{ cm}^{-1}$ and $\nu_0 \simeq 56\,000\text{ cm}^{-1}$ for sample B1, but these figures are necessarily very uncertain, as they are based only on a small part of the tail of the band, and assume a Gaussian form factor. However, the integrated intensity is very high, marking this as an interband transition, probably involving the transfer of an electron from the 1π molecular orbital (derived from the oxygen $2p$ band) to the $3-d$ bands of Fe^{2+} , i.e. photochemical reduction of Fe^{2+} to



FIGS. 1 and 2: FIG. 1 (left). Unpolarized ω -spectra of representative micas ranging in FeO content from 1.2 % (P1) to 24.8 % (L2), showing the tail of the intrinsic absorption band centred in the near ultraviolet (*A*), the composite band system at 4000 to 6000 Å (*B*), the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer band at 7200 Å (*C*), and the two *d-d* bands of Fe^{2+} at 8700 and 11500 Å (*D'*, *D''*). Note that the optical density at 5900 Å (D_{5900}) provides a measure of the intensity of band *A*. FIG. 2 (right). The unpolarized ω -spectrum of sample B1 plotted conventionally to show the transmission window (*T*) in the green, the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer band (*C*), and the two *d-d* bands of Fe^{2+} (*D'*, *D''*).

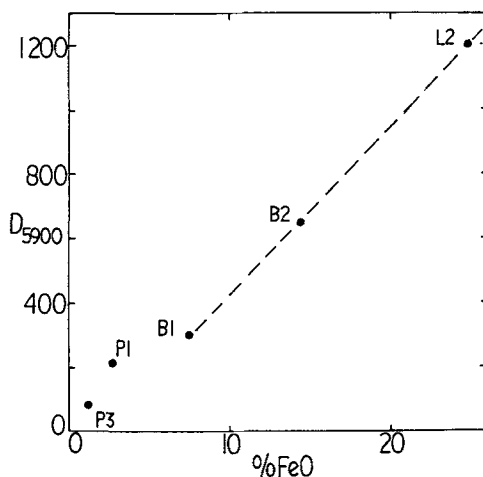


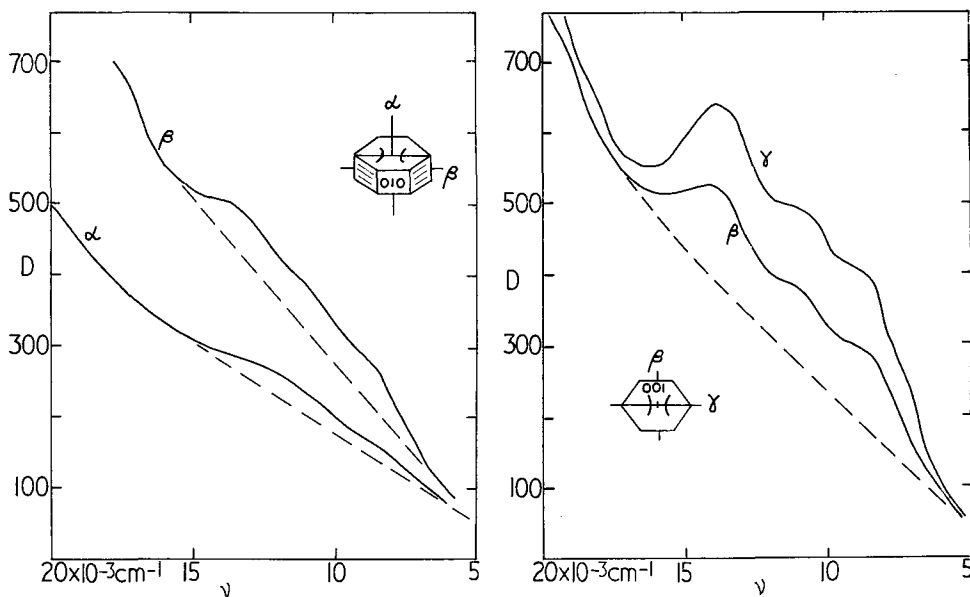
FIG. 3. Optical densities at 5900 Å plotted against FeO content for the five mica spectra in fig. 1.

Fe^{2+} . The background absorption in other iron minerals has a similar origin, but their absorption edges usually lie further into the near ultraviolet.

The polarization dependence of the absorption edge is shown in figs. 4 and 5. There is little difference between the two components of the spectra, but the $\epsilon = \alpha$ absorption edge lies at photon energies some 6000 cm^{-1} higher than the $\omega = (\beta, \gamma)$

edge. This may imply that ν_0 for the ϵ band is displaced to higher energies, or that the ω -band is broader or stronger. Measurements in the vacuum ultraviolet (1000 to 1850 Å) would be needed to resolve this point.

The 5000 Å band system: On careful inspection band B appears to be composite, and its intensity cannot easily be related to the concentration of any one ion. Both Fe_2O_3 and TiO_2 have strong intrinsic absorption bands in the 4000 Å region, and it



FIGS. 4 and 5: FIG. 4 (left). The α and β spectra of a transverse section of sample B10, showing the differing positions of the absorption edge for light vibrating with $E_{\perp}(\alpha)$ and $E_{\parallel}(\beta)$ to the (010) cleavage, and the polarization of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer band (C), which is absent from the α spectrum. FIG. 5 (right). The β and γ components of the ω spectrum of sample B2, showing the anisotropic absorption of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer (C) band, and the small displacement of the absorption edge ($\gamma > \beta$).

is probable that these contribute to B, together with several spin-forbidden bands of Fe^{2+} and Fe^{3+} , the spin-allowed $d-d$ transitions of Ti^{3+} (present in small amounts in some micas), and possibly some high-energy metal-metal charge-transfer bands. We consider that the intrinsic ($\text{O} \rightarrow \text{Ti}$) absorption of octahedrally coordinated Ti^{4+} provides the main contribution.

The 7200 Å (metal-metal) charge-transfer band

Assignment: The integrated intensity of the 7200 Å (C) band is proportional to the product of the Fe^{2+} and Fe^{3+} concentrations (fig. 6) thus confirming its assignment to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ electron transfer. The octahedra about the c and h ions in the brucite layer share edges, and electron transfer can therefore proceed either by direct exchange

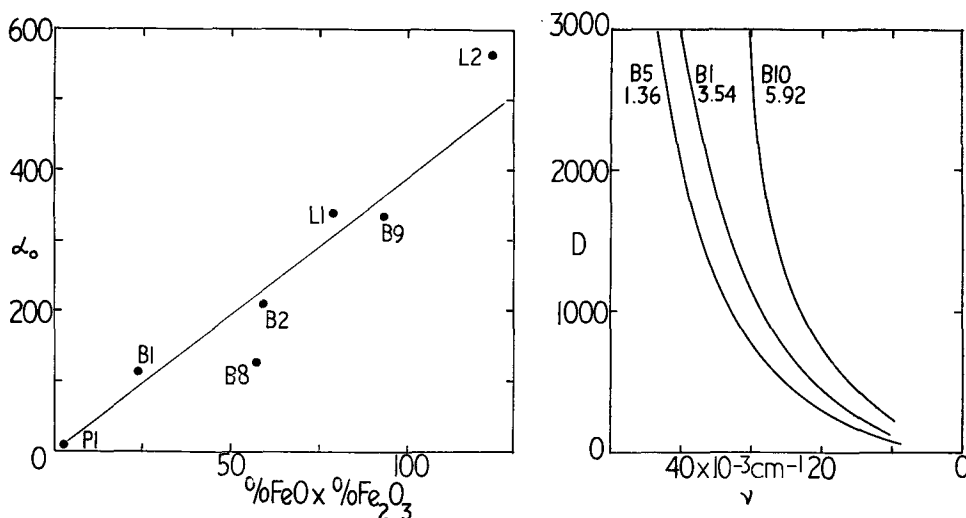
(t_{2g} - t_{2g} overlap) or indirect exchange via the oxygen $p(\pi)$ orbitals. The relative insensitivity of the oscillator strengths to metal-metal distance (Robbins and Strens, 1968a) and the observation that indirect rather than direct exchange is responsible for magnetic ordering in most oxides leads us to prefer t_{2g} - $p(\pi)$ - t_{2g} overlap as the path for electron exchange. Values of d -orbital wave-functions in oxides are uncertain, and calculations of overlap are therefore unreliable, although they have been attempted (Townsend, 1970).

Energy: There is not sufficient time for metal-oxygen distances to adjust during an electronic transition, and charge-transfer therefore leaves an Fe^{2+} ion in a site with metal-oxygen distances appropriate to Fe^{3+} , and vice versa. The energy required to compress the Fe^{2+} -O distance from 2.13 Å to 2.01 Å can be estimated as $\sim 2600 \text{ cm}^{-1}$ from the PV data of Tischer and Drickamer (1962) for FeO, whilst that needed to extend the Fe^{3+} -O distance from 2.01 Å to 2.13 Å is approximately $12\,400 \text{ cm}^{-1}$, giving a total of $\sim 15\,000 \text{ cm}^{-1}$, which compares with the observed values of $13\,600$ to $18\,000 \text{ cm}^{-1}$ for charge-transfer between octahedrally coordinated iron in a range of minerals (Robbins and Strens, 1968a). This approach implies that $h \rightarrow c$, $c \rightarrow h$, and $h \rightarrow h$ charge-transfer will occur at different energies, since the h and c sites have different metal-oxygen distances. However, the 7200 Å band appears symmetrical, so that the differences in ν_0 are either small compared with $w_{\frac{1}{2}}$, or not all the possible components are seen (see below).

Polarization: The 7200 Å band is present in both β and γ components of the ω -spectra, but absent from the $\epsilon = \alpha$ spectra of all samples examined in transverse section, implying that the transition moment lies in the plane of the brucite layer (fig. 4). This is consistent with our previous finding (Robbins and Strens, 1968a) that the transition moment of metal-metal charge-transfer bands was directed rather accurately along the metal-metal vector. It is more difficult to account for the anisotropy of the β and γ components of the ω spectra (fig. 5), for which A_{γ}/A_{β} ranges from 2.0 in B2 to 2.5 in B5. Each h or c ion is surrounded by six nearest-neighbour cations in hexagonal array at a distance of 3.1 Å in the (001) plane, there being a total of $6hc + 6ch + 6hh$ contacts per formula unit. The metal-metal vectors corresponding to each of these three sets of contacts are disposed with pseudo-trigonal symmetry, and could not contribute greatly to the anisotropy unless there is some degree of inequivalence within and between sets. Now, each h or c ion is coordinated by four oxygens (each linked to $1\text{Si} + 2h + 1c$ ions) and two hydroxyls (each linked to $2h + 1c$ ions). If electron transfer occurs via oxygen $p(\pi)$ orbitals as we suggest, and if the probability of electron transfer is greater for OH^- than for O^{2-} ions, then a mechanism exists that allows anisotropy of the type observed. There are $4hc$, $4ch$, and $4hh$ contacts involving bridging OH^- ions, for which the polarizations predicted are: hh , γ 4, β 0, with shared edge 2 OH^- ; ch and hc , γ 1, β 3, with shared edge OH^- and O^{2-} . The observed intensity ratio A_{α}/A_{β} of 2.0 to 2.5 would correspond to a transition probability for hc and ch contacts some 40 % of that for hh , if the cation distribution is similar to that in the Aberdeen biotite. This interpretation may appear speculative, but the idea that transfer via hydroxyl is easier than transfer via oxygen is supported

by the observation that charge transfer bands in hydrous iron silicates (biotite, chlorite, tourmaline) are much more prominent than in anhydrous silicates with structures that appear equally favourable to their development (e.g. pyroxene), and the apparent difference in transfer probability for edge and corner sharing also seems reasonable.

Intensity: From fig. 6 it will be seen that the intensity of the 7200 Å band is given approximately by the relation $\alpha_0 \simeq 4(\% \text{ FeO} \times \% \text{ Fe}_2\text{O}_3) \text{ cm}^{-1}$. Other things being equal, the intensity of a metal-metal charge-transfer band is determined by the number



FIGS. 6 and 7: FIG. 6 (left). Plot of the absorption coefficient at band maximum (α_0) of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer band (*C*) against the product ($\% \text{ FeO} \times \% \text{ Fe}_2\text{O}_3$), for seven micas for which ω -spectra showed good resolution of the *C*-band. Part of the scatter is attributed to the fact that the β and γ vibration directions were not defined relative to the partially polarized light beam, so that the nominally unpolarized ω -spectra of different samples will in practice contain slightly different amounts of the β and γ components. FIG. 7 (right). The effect of increasing TiO_2 contents on the ω -absorption edge of three micas containing comparable amounts (7 to 8%) of FeO, after removing absorption by bands *B*, *C*, *D'*, and *D''*.

of donor-acceptor pairs, which in turn depends on the product of the donor and acceptor concentrations, multiplied by the number of contacts. If the contacts are inequivalent, this product must be weighted by the transfer probability via each type of contact.

Robbins and Strens (1968*a*) derived relations for the oscillator strength and extinction coefficient of metal-metal charge-transfer bands, assuming that all contacts[†] contributed equally:

$$f_{ij} = (mc^2/\pi Ne^2) \cdot A_{ij}V/(6ch + 6hc + 6hh) \quad (1)$$

[†] The number of contacts is incorrectly given as 32 for a formula unit containing six *h*+*c* ions in table I of this reference; the correct number is 36.

where hc , ch , hh are the appropriate products of mole fractions of donor and acceptor ions in the sites indicated, $A_{\parallel} = A_{\beta} + A_{\gamma} \simeq 2A\omega$, and V is the molar volume. The first term on the right-hand side has the value 1.877×10^{-12} where both $w_{\frac{1}{2}}$ and α_0 are expressed in cm^{-1} in the calculation of A . Assuming a random distribution of donor (Fe^{2+}) and acceptor (Fe^{3+}) ions, and 18 contacts per formula unit, equation (1) yields $f \simeq 0.003$ for most samples. Changes in cation distribution have relatively little effect on this figure over the composition range of interest. If allowance is made for the inequivalence of hc , ch , and hh contacts, we find $f_{hc} = f_{ch} \simeq 0.003$ and $f_{hh} \simeq 0.008$. The extinction coefficient is given by: $\epsilon = D_{\parallel}V/1000[c]$ where $[c]$ is the denominator of equation (1). Note that to accord with usage by chemists, ϵ has been expressed in terms of optical density rather than absorption coefficient. The values of ϵ corresponding to the oscillator strengths found above range from 130 to 180 for a random distribution and 18 contacts per formula unit. These figures are changed to $\epsilon_{hc} = \epsilon_{ch} \simeq 150$, and $\epsilon_{hh} \simeq 400$ when allowance is made for the inequivalence of the various contacts. Comparison is made with the intensity of $d-d$ and $\text{O} \rightarrow \text{Fe}^{2+}$ bands in Table II.

The 9200 and 11 500 Å bands

Assignment: The integrated intensities of the 9200 and 11 500 Å bands obtained by deconvolution of the ω spectra are directly proportional to the FeO content (Robbins, 1967), and they are assigned to internal $d-d$ transitions of the Fe^{2+} ions, in which electrons are transferred from the t_{2g} orbital of lowest energy to e_g levels resolved by distortion of the octahedra about the h and c ions. The nature of this distortion is uncertain, but calculations based on atomic coordinates in phlogopite (Steinfink, 1962) and annite (Donnay *et al.*, 1964) suggest that it would split the e_g levels of Fe^{2+} ions on both h and c sites by some 2000 cm^{-1} , thus quenching the dynamic Jahn-Teller effect (Cotton and Myers, 1960).

Energy: The transition energies obtained from the computer fitting of the spectra are rather larger than is usual for iron compounds, suggesting that the Fe-O distances are shortened. The average radius of the cations in the brucite layer is less than that of Fe^{2+} , and some compression seems likely.

Polarization: The experimental values of the ratios A_{ϵ}/A_{ω} are unreliable, owing to the poor quality of the ϵ spectra, but there is a definite anisotropy of the $d-d$ bands for vibration directions in the plane of the cleavage flake, with $A_{\gamma} > A_{\beta}$.

Intensity: Extinction coefficients calculated for the D' and D'' bands are 23 and 28 respectively for sample B1, and lie within the normal limits for spin-allowed $d-d$ transitions (Table II).

Solid solution effects

Under this heading are considered certain features that are observed in the spectra of mixed crystals, although they are not present in those of the end-members. Since the brucite layer of biotite is a six-component solid solution of ions ranging in charge from zero (\square) to four (Ti) and in metal-oxygen distance from 1.9 Å (Al) to 2.2 Å (\square),

such effects as substitutional broadening and substitutional intensification of absorption bands are to be expected.

Substitutional broadening: Each *c* or *h* cation in the brucite layer is surrounded by six (*6h* or *3c+3h*) nearest neighbours in hexagonal array at a distance of 3.1 Å in the (001) plane. Consider a reference cation in the brucite layer: in a random six-component solid solution the six nearest neighbours of this ion may be chosen in

TABLE II. *Spectral parameters of absorption bands in representative micas*

Band		P1	B1	B2	L2
A	D_{5900}	115	300	650	1200 cm ⁻¹
	FeO	2.71	7.46	14.41	24.75 %
C	ν_0	13.90	13.66	13.71	13.86 × 10 ³ cm ⁻¹
	$w_{\frac{1}{2}}$	—	3.40	3.67	3.95 × 10 ³ cm ⁻¹
	D_0	9	114	210	567 cm ⁻¹
	$A_{ }$	—	2.2	4.5	13 × 10 ⁶
	$f_{ }$	(0.002)	0.003	0.002	0.003 per ion pair
	C'	2.6	23	59	124 (% FeO × % Fe ₂ O ₃)
D'	ν_0	11.18	10.92	10.97	10.98 × 10 ³ cm ⁻¹
	D_0	6.4	75	112	219 cm ⁻¹
	ϵ_0	5.6	23.3	17	19 l mole ⁻¹ . cm ⁻¹
D''	ν_0	8.46	8.55	8.76	8.96 × 10 ³ cm ⁻¹
	D_0	6.8	90	168	368 cm ⁻¹
	ϵ_0	6.0	28	26	31 l mole ⁻¹ . cm ⁻¹

6⁶ = 46 656 ways, comprising 6 + 6 × 5 + . . . + 6! = 1956 chemically distinct configurations, each of which is characterized by a multiplicity ranging from 6 to 6! = 720. Each of the 1956 configurations corresponds to a particular set of electronic energy levels of the reference ion, and the observed absorption envelope thus represents the sum of 1956 bands, each of slightly different energy. Absorption bands should therefore be broader in biotite than in phlogopite, and in general broader in any intermediate member of a solid solution than in a pure end-member. In biotites, the effect of titanium substitution is particularly marked (fig. 7), causing the intrinsic (O → Fe²⁺) absorption band to broaden and encroach on the visible region.

We attribute the strong absorption in the visible region of the biotite spectrum to substitutional broadening, and suggest that different degrees of broadening of the ϵ and ω intrinsic absorption bands provide the most probable explanation of the difference in energy of the corresponding absorption edges (fig. 4).

Substitutional intensification: The intensity of an electric dipole transition, for example the *d-d* and charge-transfer transitions discussed in this paper, is given by an expression of the type: $A \propto \langle \psi_g | \mu_x | \psi_e \rangle$, where ψ_g and ψ_e are the wavefunctions of the ground and excited states, and μ_x is the dipole moment in the *x* direction (Dodd, 1962). The transition will clearly have zero intensity if either ψ_g , ψ_e or μ_x is zero, but we are concerned here only with the magnitude of the dipole moment. The simplest

cases are those of the $d-d$ transitions of an ion located on various symmetry elements. The dipole moment is zero for all polarizations if a centre of symmetry is present, and also for directions normal to a mirror plane or rotation axis of even order. Thus some transitions for which ψ_o/ψ_e is finite will none the less be forbidden for some or all polarizations. At higher temperatures, atomic vibrations generate transient dipole moments, and the transition will occur weakly. These 'vibronic' bands are typically broad and weak, and their integrated intensity increases with temperature.

Now a dipole moment represents the product of a separation and a charge, and any deviation of a structure from its ideal configuration that involves changes in the separation or charge of the ions in the structure may give rise to permanent dipole moments. For example, the introduction of smaller or larger ions, or the occurrence of heterovalent substitutions, will cause local distortions or charge imbalances, and thus generate dipole moments, which will often be larger than the transient dipoles responsible for vibronic bands. The transient and permanent contributions can be resolved by cooling the sample to a temperature at which vibronic coupling becomes unimportant. The effect is in general to permit in solid solutions or other 'imperfect' crystals transitions that would not be allowed in the ideal end-members. This mechanism may be responsible for the increased strength of the D' and D'' bands in biotite as compared with phlogopite (Table II).

Discussion and conclusions

Both the colour and the pleochroism of biotites are simply related to the main features of the absorption spectra. The colour of light transmitted through cleavage flakes of a mica containing FeO and Fe₂O₃, but no TiO₂, is determined by the presence in the visible region of the tail of the O → Fe²⁺ charge-transfer band, which cuts out the blue light, and by the Fe²⁺ → Fe³⁺ charge-transfer band at 7200 Å, which absorbs in the red and yellow, leaving a transmission window in the green (fig. 2). Addition of TiO₂ causes the O → Fe²⁺ band to broaden (fig. 7), but leaves the Fe²⁺ → Fe³⁺ band relatively unaffected, causing the transmission window to become shallower and the transmitted light to take on a reddish-brown colour. This behaviour is in general agreement with Hayama's (1959) findings.

The strong pleochroism is related to the same spectral features. The difference between ϵ and ω vibration directions arises because the absorption edge lies further into the visible in the ω spectra, and the strong Fe²⁺ → Fe³⁺ charge-transfer band is also polarized in this plane. The result is much stronger absorption of all wavelengths for vibration directions in the plane of the cleavage flake. The minor differences between the β and γ components of the ω spectra are attributable to a slight anisotropy of both the Fe²⁺ → Fe³⁺ and O → Fe²⁺ bands, but the effect is almost imperceptible in most samples.

The very great differences between the intensities of the various absorption bands (table II) may be understood using a model described by Dodd (1962). The oscillator strength of a transition of wavenumber ν involving a redistribution of charge equivalent to one electron over a distance r is given by: $f = 2\pi^2 m c \nu r^2 / 3000h = 1.5r^2\nu \times 10^{-6}$

where r and ν are in Å and cm^{-1} respectively. Since r and ν are known, or can be estimated, for bands A , C , D' , and D'' , it is possible to compare observed and calculated f -values (Table III). The agreement is reasonable for the three bands involving strongly-bonded atoms (A) and internal transitions (D' , D''), but the calculated f -value of the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge-transfer band is very much larger than that observed, reflecting the indirect nature of the transition.

TABLE III. Comparison of observed and calculated oscillator strengths

Band	r	ν	$w_{\frac{1}{2}}$	f_{calc}	f_{obs}
A	2.1 Å	$56.0 \times 10^3 \text{ cm}^{-1}$	$4.3 \times 10^3 \text{ cm}^{-1}$	0.36	0.12
C	3.1	13.7	3.5	0.20	0.003*
D'	(0.2)†	10.9	2.1	0.0006	0.0003
D''	(0.2)†	8.6	1.7	0.0005	0.0004

* Assuming random cation distribution, $n = 18$. † Estimated.

Both the substitutional effects seen in the biotite spectra are favoured by heterovalent substitutions, and by those homovalent replacements that involve ions differing markedly in radius. Substitutional broadening of the $\text{O} \rightarrow \text{Fe}^{2+}$ band is probably responsible for the strong absorption in the visible region by many iron minerals, including schorl, basaltic hornblende, and kaersutite, as well as biotite and aluminous orthopyroxene. Similar broadening also occurs in other types of spectra, e.g. infrared and Mössbauer.

Substitutional intensification should be most easily detected in the $d-d$ spectra of transition-metal ions occupying coordination polyhedra of high symmetry, particularly those with centres of symmetry. At room temperature the r.m.s. amplitude of atomic vibrations in minerals is of the order of 1 % of the metal-oxygen distance, and substitutionally- and vibronically-allowed bands should thus be comparable in strength when substitutions cause distortions of the order of 1 % of the bond-length, or change the effective charges on the ligands by the same amount.

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