

RACAH PARAMETERS AND THEIR RELATIONSHIP TO LENGTHS AND COVALENCIES OF Mn^{2+} - AND Fe^{3+} -OXYGEN BONDS IN SILICATES

P. G. MANNING*

ABSTRACT

The energies of the Russell-Saunders states 4G and 4D in Fe^{3+} and Mn^{2+} in a number of silicates have been determined from the identification of the field-independent transitions ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ and ${}^6A_1 \rightarrow {}^4E(D)$. Absorption bands marking these transitions are relatively sharp, which aids in their identification.

The separations of the 6S_1 , 4G and 4D levels are reduced in the bonded ions. Racah parameters have been calculated, and the B -parameters of Fe^{3+} , in particular, in three garnets, kyanite, vesuvianite and muscovite are discussed in terms of metal-oxygen covalency and, in turn, metal-oxygen distance. B -values are also reported for Fe^{3+} in tetrahedral sites in orthoclase.

INTRODUCTION

The ${}^4A_1 {}^4E(G)$ and ${}^4E(D)$ levels derived from the Russell-Saunders states 4G and 4D in the $3d^5$ ions Mn^{2+} and Fe^{3+} are field-independent, and absorption bands marking electronic transitions to these levels from the ${}^6A_1(S)$ ground state are often easily identified by their sharpness. It is invariably found that the separations between the Russell-Saunders states are smaller in the complexed ion than in the free ion, *e.g.*, for Fe^{3+} in andradite the 4G level is at $22,700 \text{ cm}^{-1}$ (Manning 1967*b*) whereas the free-ion value is $32,800 \text{ cm}^{-1}$ (Moore 1952). Because the separations between the states are due to repulsions between the d electrons, the smaller separations in complexes suggest that the mean distance between the electrons has increased, *i.e.*, the electron cloud has expanded. This expansion of the d -electron clouds has been termed the nephelauxetic effect (Jorgensen 1962, 1966) and is attributable at least in part to metal-anion orbital overlap.

Jorgensen has suggested that the ratio, β , of the Racah B -parameter of the bonded cation to the B -parameter of the free ion is a measure of metal-anion covalency. The Racah B and C parameters describe the effects of inter-electron repulsion. Assuming $C = 4B$, Jorgensen calculated from the energy of the ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ transition in Fe^{3+} oxalate, fluoride and H_2O complexes, β values of 0.68 to 0.78. For $\text{Mn}(\text{OH}_2)_6^{2+}$, Jorgensen calculated a value of $\beta = 0.93$, showing that the Fe^{3+} complexes

*Research Scientist, Inland Waters Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

are more covalent than the Mn^{2+} , a reasonable conclusion. However, Keester & White (1966) have shown that for Mn^{2+} in a number of minerals, the C/B ratio can vary markedly. They calculated values of B and C from the expressions:

$$\nu_1 = E(^4A_1, ^4E(G)) - E(^6A_1(S)) = 10B + 5C$$

and
$$\nu_2 = E(^4E(D)) - E(^6A_1(S)) = 17B + 5C$$

which are solutions of the Tanabe-Sugano equations. For $\text{Mn}(\text{OH}_2)_6^{2+}$ $\beta = 79$, and for a number of silicates $\beta = 73-83$. Berkes (1968) has reported energy level diagrams for d^5 ions for various values of B and C , and one of his diagrams is reproduced in Figure 1.

The energies of the 4G and 4D levels in the free-ion are $32,800 \text{ cm}^{-1}$ and $38,500 \text{ cm}^{-1}$ for Fe^{3+} and $26,850 \text{ cm}^{-1}$ and $32,350 \text{ cm}^{-1}$ for Mn^{2+} (Moore 1952). Hence, for Fe^{3+} the free-ion B -value (B_0) is 814 cm^{-1} and for Mn^{2+} $B_0 = 785 \text{ cm}^{-1}$.

In the current study, β -values are reported for Mn^{2+} and Fe^{3+} in octahedral sites in a number of silicates, together with the β -value for Fe^{3+} in tetrahedral sites in orthoclase. The Racah parameters are calculated from the above solutions of the Tanabe-Sugano equations, namely $\nu_2 - \nu_1 = 7B$. The study suggests that B -values could prove useful in determining relative sizes of Fe^{3+} sites in minerals.

EXPERIMENTAL

Spectra were recorded using a Beckman DK-2A spectrophotometer; experimental details are as described in earlier works (Manning 1967a).

DISCUSSION

Spectra of Mn Silicates

Values of ν_1 , ν_2 and the Racah parameters for Mn^{2+} in silicates determined by the author are presented in Table 1. Some of the spectra have been reported earlier (Manning 1968a), while the spectra of the others are sufficiently conventional that they will not be reported here.

Garnets

Relevant portions of the absorption spectra of almandine, pyrope, spessartine and grossular are presented in Figure 2. The complete spectra and their interpretations have been reported earlier (Manning 1967a for pyrospites; Manning 1969 for ugrandites). The $7,800 \text{ cm}^{-1}$ bands are definitely spin-allowed bands of 8-coordinate Fe^{2+} , but the identities of the $\sim 27,000 \text{ cm}^{-1}$ bands in pyrospites have still to be confirmed.

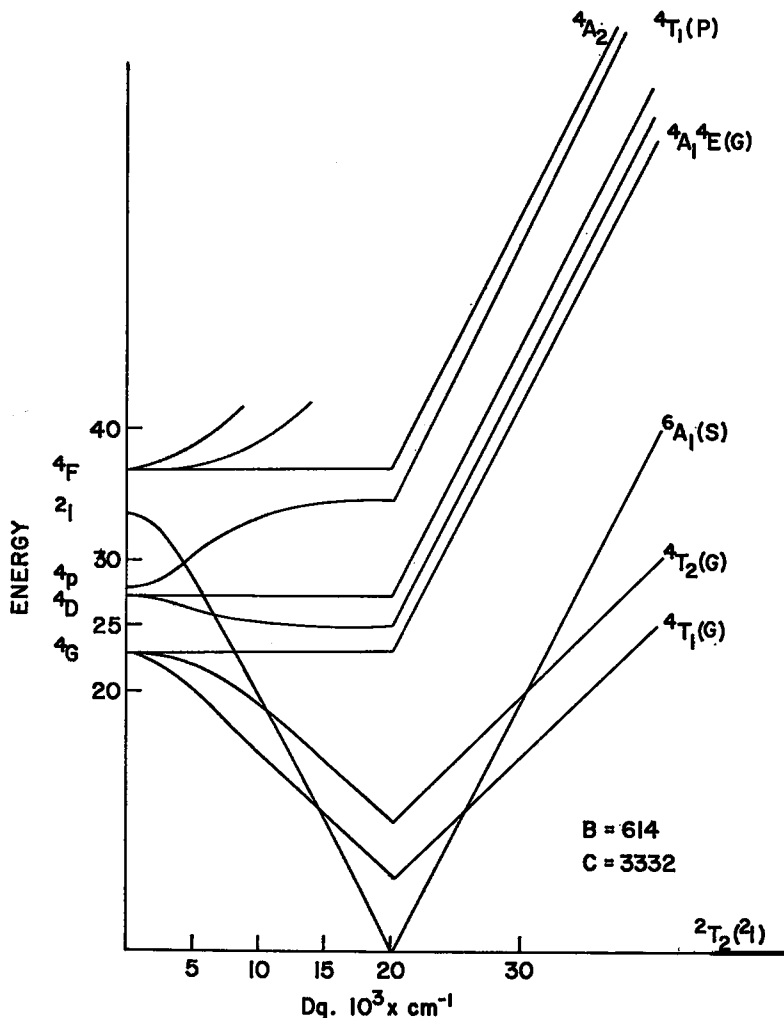


FIG. 1. Energy level diagram for d^5 ions in cubic fields (Berkes 1968).

In Table 2 are listed the ratios of the absorbance of the $7,800\text{ cm}^{-1}$ band to the absorbance of the $27,000\text{ cm}^{-1}$ band for the pyralspites described earlier (Manning 1967a). The ratios clearly indicate that the $27,000\text{ cm}^{-1}$ bands in pyralspites are not Fe^{2+} bands. However, the similar energies and shapes of the $27,000\text{ cm}^{-1}$ bands in pyralspites and grossulars suggest a common origin, namely, they mark transitions to the second field-independent state ${}^6A_1 \rightarrow {}^4E(D)$ (Manning 1969) in Fe^{3+} .

TABLE 1. RACAH PARAMETERS FOR Mn^{2+} IN SILICATES (energies in cm^{-1})

Mineral	$10^{-3}\nu_1$	$10^{-3}\nu_2$	B	C	C/B	β
Pyroxmangite [(Mn, Fe)SiO ₃]	24.3	29.0	671	3520	5.25	0.85
Rhodonite (MnSiO ₃)	24.25	29.0	679	3490	5.15	0.86
Bustamite* [(Mn, Ca)SiO ₃]	24.4	29.05	664	3540	5.35	0.85
Serandite (Na ₈ (Ca, Mn) ₁₅ Si ₂₀ O ₅₈ .2H ₂ O)	24.55	29.3	679	3550	5.25	0.86
Penwithite (MnSiO ₂ .2H ₂ O)	24.5	29.2	671	3560	5.30	0.85
Schefferite	24.2	—	—	—	—	—
Friedelite [(Mn, Fe) ₈ Si ₆ O ₁₅ OH ₁₀]	24.65	29.2	650	3630	5.60	0.83
Ganophyllite (Mn ₇ Al ₂ Si ₅ O ₂₆ .6H ₂ O)	24.45	29.05	657	3580	5.45	0.84

*The 4A_1 and 4E levels are not resolved.

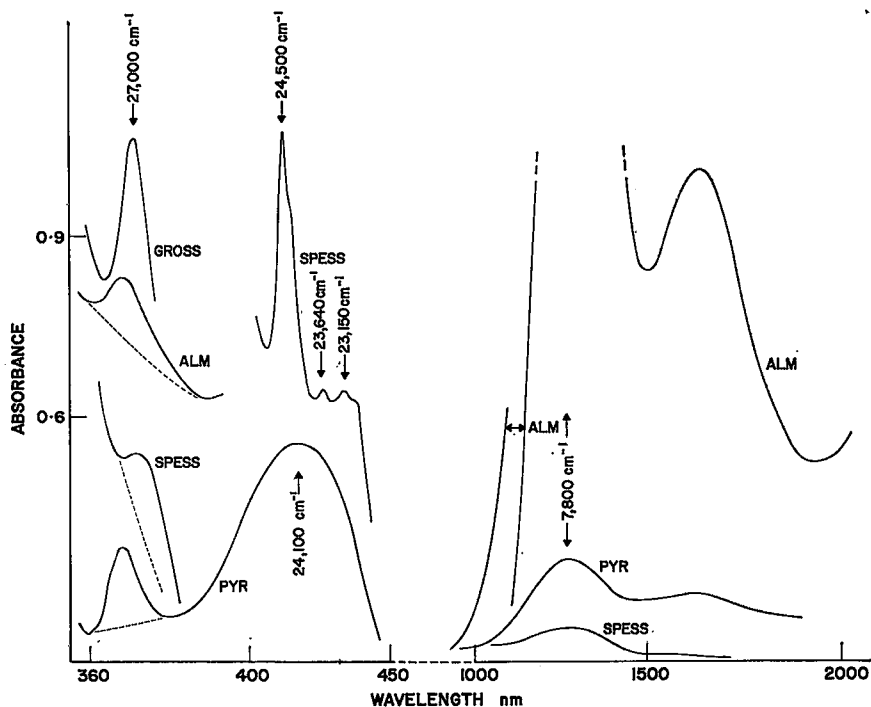


FIG. 2. Partial optical absorption spectra of garnets. ALM = almandine, SPESS = spessartine, GROSS = grossular.

TABLE 2. ABSORBANCE RATIOS FOR PYRALSPITES

Mineral	Location	$A(7,800)$	$A(27,000)$	Ratios
Almandine	Madagascar	1.7	0.10	17
Almandine	Gore Mtn.	0.78	0.17	4.6
Pyrope	Czechoslovakia	0.15	0.14	1.1
Spessartine	Parry Sound	0.04	0.15	0.25

TABLE 3. RACAH PARAMETERS FOR Fe^{3+} IN SILICATES (energies in cm^{-1})

Mineral	$10^{-3}\nu_1$	$10^{-3}\nu_2$	B	C	C/B	β
Spessartine*	23.4	26.9	500	3680	7.35	0.61
Grossular	23.1	27.0	557	3505	6.30	0.68
Andradite*	22.85	27.0	593	3365	5.65	0.73
Kyanite*	22.9	27.0	585	3410	5.85	0.72
Vesuvianite	21.6	26.0	630	3060	4.85	0.77
Muscovite	22.6	27.3	670	3180	4.75	0.82
Orthoclase**	22.65	26.5	550	3420	6.20	0.68

* ν_1 is average energy of 4A_1 and 4E levels.

**Tetrahedral.

The 4A_1 ${}^4E(G)$ levels of Fe^{3+} in andradites and grossulars have been identified in earlier works (Manning 1967*b*, 1969). The ν_1 , ν_2 , B , C and β values for andradites and grossulars are listed in Table 3. The ν_1 -values for pyralspites have not been positively determined, although it was suggested (Manning 1967*a*) that a very weak band at $21,800\text{ cm}^{-1}$ in almandine spectra could mark the transition to the 4A_1 ${}^4E(G)$ level. The absorbance ratios in Table 2 suggest that weak Fe^{3+} bands are most likely to be observed in spessartine spectra because here the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio is greatest. The solubility of Fe^{3+} in spessartine is likely to be greater than in almandine or pyrope because the larger cell-size promotes substitution of Fe^{3+} for the smaller Al^{3+} (Burns & Strens 1967).

The two very sharp peaks at $23,150\text{ cm}^{-1}$ and $23,640\text{ cm}^{-1}$ in spessartine spectra (Fig. 2) are strongly indicative of the ${}^6A_1 \rightarrow {}^4A_1$ ${}^4E(G)$ transition in Fe^{3+} . Based on 1% Fe^{3+} content the ϵ -value of the peaks is ~ 1 ; the separation of the peaks is also very reasonable. These two peaks cannot reasonably be assigned to Mn^{2+} in view of the fact that the 4A_1 ${}^4E(G)$ levels in Mn^{2+} are very prominent at $24,500\text{ cm}^{-1}$. The ${}^6A_1 \rightarrow {}^4A_1$ ${}^4E(G)$ transition in Fe^{3+} in pyrope is unfortunately "swamped" by the intense Cr^{3+} band at $24,100\text{ cm}^{-1}$.

Muscovite

The absorption spectrum of Fe^{3+} in muscovite (Faye 1968; Manning 1969) is similar to that in andradite, $\nu_1 = 22,600\text{ cm}^{-1}$ and $\nu_2 = 27,300$

cm^{-1} . In view of the fact that the muscovite studied by Manning contained 6% Fe^{3+} and only traces of Fe^{2+} and Mn^{2+} , these assignments are considered reliable.

Kyanite

The absorption spectra of green kyanite have been reported by White & White (1967) and Faye & Nickel (1969), the latter's spectrum being resolved to higher energies. Sharp bands marking transitions to the ${}^4A_1 {}^4E(G)$ levels in Fe^{3+} are easily identified at $22,400 \text{ cm}^{-1}$ and $23,400 \text{ cm}^{-1}$. Faye & Nickel report two sharp peaks at $26,500 \text{ cm}^{-1}$ and $27,000 \text{ cm}^{-1}$ which they assign to the ${}^6A_1 \rightarrow {}^4T_2(D)$ transition. No other absorptions are visible up to $28,600 \text{ cm}^{-1}$.

Taking the average energy of the ${}^4A_1 {}^4E(G)$ levels, the ${}^6A_1 \rightarrow {}^4E(D)$ transition in Fe^{3+} should be observed below $22,900 + 7B_0 \text{ cm}^{-1}$, *i.e.*, $28,600 \text{ cm}^{-1}$. Therefore, either the $26,500 \text{ cm}^{-1}$ or the $27,000 \text{ cm}^{-1}$ band marks the second field-independent state. Because the ${}^4T_2(D)$ state is at a lower energy than the ${}^4E(D)$, then $\nu_2 = 27,000 \text{ cm}^{-1}$. The Racah parameters are listed in Table 3.

Idocrase

Absorption spectra of idocrase have been reported by Grum-Grzhimailo and coworkers (1963) and Manning (1968*b*). Both make $\nu_1 = 21,600 \text{ cm}^{-1}$, hence $\nu_2 \gtrsim 27,300 \text{ cm}^{-1}$. Manning (1968*b*) reports a prominent band at $26,000 \text{ cm}^{-1}$ on the limb of the ultraviolet absorption edge, which could very reasonably be ν_2 . The Racah parameters are listed in Table 3.

Orthoclase

The absorption spectrum of tetrahedrally-bonded Fe^{3+} in orthoclase, in which Fe^{3+} substitutes for Al^{3+} , was recently reported by Faye (1969) and is reproduced in Fig. 3. Faye tentatively assigned the very sharp $26,500 \text{ cm}^{-1}$ band to transitions to the field-independent levels ${}^4A_1 {}^4E(G)$. The $24,000$ and $22,650 \text{ cm}^{-1}$ bands were then assigned to transitions to the ${}^4T_2(G)$ and ${}^4T_1(G)$ levels respectively, and the $20,700 \text{ cm}^{-1}$ band to some other transition-metal ion.

The ${}^4A_1 {}^4E(G)$ levels are not exactly degenerate, and in well-resolved spectra of Mn^{2+} and Fe^{3+} (Manning 1967*b*; 1968*a*) the 4A_1 and 4E appear as two peaks, or peak-and-shoulder, with separations of $300\text{--}1,000 \text{ cm}^{-1}$. The orthoclase crystal was thinned to 0.02 cm , but no absorption was detected at energies up to $33,000 \text{ cm}^{-1}$. Therefore the $26,500 \text{ cm}^{-1}$ band cannot mark transitions to either the ${}^4A_1 {}^4E(G)$ or ${}^4T_2(D)$ levels because $7B_0 = 5,700 \text{ cm}^{-1}$ and $26,500 + 5,700 < 33,000$. However, the sharpness

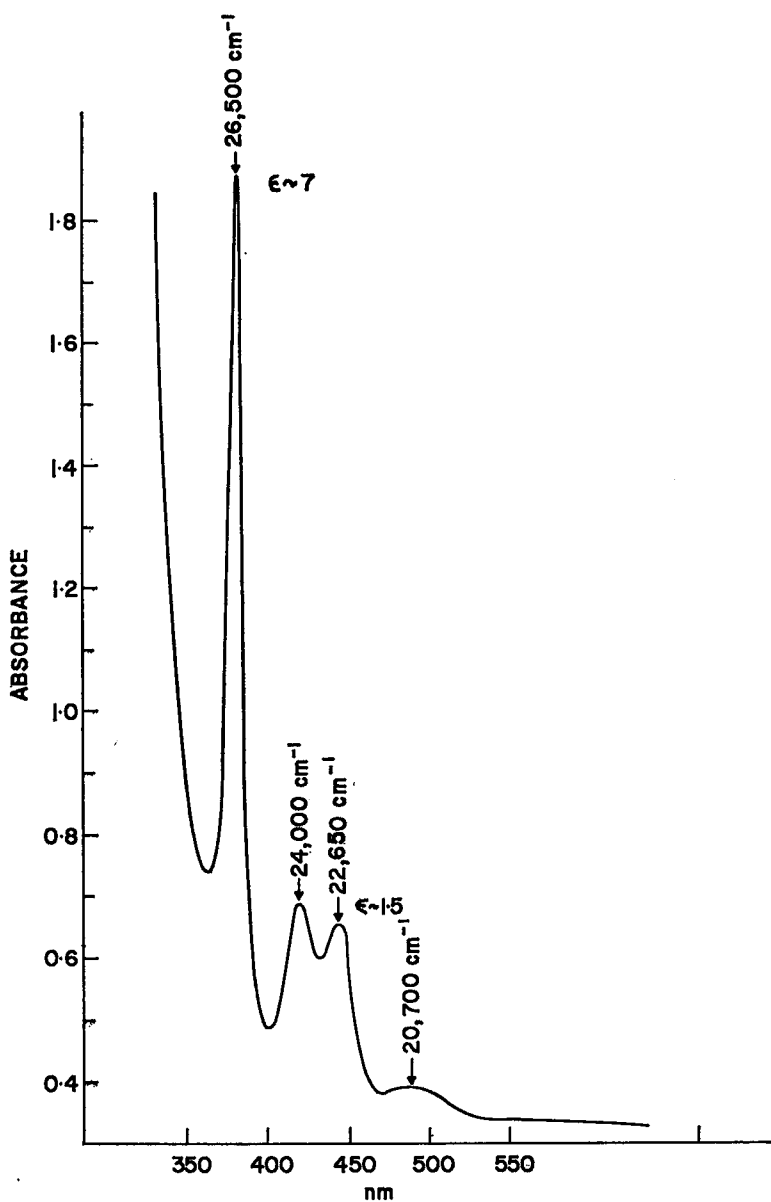


FIG. 3. Absorption spectrum of orthoclase (Faye 1969). Sample thickness = 0.32 in.

of the $26,500\text{ cm}^{-1}$ band does suggest transitions to a field-independent state, probably ${}^4A_1 \rightarrow {}^4E(D)$. If this is so, then the ${}^4A_1{}^4E(G)$ levels must occur above $21,000\text{ cm}^{-1}$, hence either or both the $22,650\text{ cm}^{-1}$ and $24,000\text{ cm}^{-1}$ bands represent transitions to these levels.

The separation of the $22,650\text{ cm}^{-1}$ and $24,000\text{ cm}^{-1}$ bands seems rather large for a splitting of the 4A_1 and 4E levels (Manning 1967*b*; 1968*a*), although they are split by $1,000\text{ cm}^{-1}$ in octahedral sites in kyanite. It is more likely that the $24,000\text{ cm}^{-1}$ band marks the transition ${}^6A_1 \rightarrow {}^4T_2(D)$; the ${}^4T_2(D)$ level is not steeply sloping in the energy-level diagram (Berkes 1968). Significantly, Faye & Hogarth (1969) have assigned a prominent absorption at $22,700\text{ cm}^{-1}$ in the spectrum of phlogopite to the ${}^4A_1{}^4E(G)$ levels in tetrahedrally-bonded Fe^{3+} . Hence, if $\nu_1 = 22,650\text{ cm}^{-1}$ and $\nu_2 = 26,500\text{ cm}^{-1}$, $B = 550\text{ cm}^{-1}$ and $C = 3,420\text{ cm}^{-1}$. It seems reasonable to assign the $20,700\text{ cm}^{-1}$ band to the ${}^6A_1 \rightarrow {}^4T_2(G)$ transition in Fe^{3+} . However, if $\nu_1 = 23,300\text{ cm}^{-1}$, $B = 460\text{ cm}^{-1}$ and $C = 3,740\text{ cm}^{-1}$.

The intensities of the bands in Fig. 3 increase markedly as they move closer to the ultraviolet, showing that the $d-d$ bands borrow intensity from $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer bands. For this reason, the band marking transitions to the lowest excited level in Fe^{3+} , ${}^4T_1(G)$, is likely to be very weak; in fact a very weak absorption is observed at $\sim 19,000\text{ cm}^{-1}$ in spectra of the thicker section of orthoclase.

GENERAL DISCUSSION

The B -values for octahedrally-bonded Mn^{2+} in the silicates listed in Table 1 range from 650 to 679 cm^{-1} , from which β -values of 0.83 and 0.86 are derived. Keester & White (1966) report B -values of 654 cm^{-1} for inesite and 590 cm^{-1} for rhodonite, the former value agrees with the B -values determined here while the latter value is incorrect. Of great interest is that Keester & White report considerably smaller B -values for glaucocroite and tephroite, 588 and 577 cm^{-1} respectively, thus implying greater covalency for Mn^{2+} bonds in these minerals.

The estimated uncertainty in the currently measured B -values is $\pm 15\text{ cm}^{-1}$, hence the relative smallness of the B -values for glaucocroite and tephroite can be considered significant. Bingham & Parke (1965) calculate Mn^{2+} B -values of 700 cm^{-1} in phosphate glasses, 630 cm^{-1} in borate glasses and 620 cm^{-1} in silicate glasses, which in conjunction with the values of Keester & White indicate the following order of Mn^{2+} -O covalency: phosphate < borate $\leq$ silicate. According to Bingham & Parke, the spectra of Mn^{2+} in silicate glasses indicate tetrahedral bonding, but they may have misinterpreted the two sharp features at $\sim 23,000\text{ cm}^{-1}$ which could well mark the ${}^4A_1(G)$ and ${}^4E(G)$ levels and not the ${}^4A_1{}^4E(G)$ and ${}^4T_2(G)$.

The β -values for Fe^{3+} in silicates (Table 3) are in general smaller than those for Mn^{2+} , which leads to the reasonable conclusion that $\text{Fe}^{3+}\text{-O}$ bonds are more covalent than $\text{Mn}^{2+}\text{-O}$: covalency generally increases with increasing cation valency. Because the B -values for the Fe^{3+} -containing silicates show a greater range than those of Mn^{2+} and, further, because the structures of the Fe^{3+} -containing silicates are known in greater detail and are also in some cases very similar, the Fe^{3+} B -values seem more amenable to discussion.

No previous B -values seem to have been reported for Fe^{3+} , in fact it is only recently that the d - d spectra of Fe^{3+} have been resolved to energies approaching the ultraviolet. The Fe^{3+} B -values increase in the order spessartine < grossular < andradite, which is the order of increasing cell-size and, further, increasing $\text{Fe}^{3+}/\text{Al}^{3+}\text{-O}$ distances. The $\text{Al}^{3+}\text{-O}$ distances in pyrope (1.89 Å; Zemann & Zemann 1961) are considerably smaller than in grossular (1.95 Å; Abrahams & Geller 1958). Quite reasonably, therefore, $\text{Fe}^{3+}\text{-O}$ covalency is related to the $\text{Fe}^{3+}\text{-O}$ distances.

For a series of minerals of similar structure, the effect of cation composition could change the electronic distribution about an oxygen and hence affect $\text{Fe}^{3+}\text{-O}$ covalency. For grossular and andradite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ and $\text{Ca}_3\text{Fe}_2^{3+}(\text{SiO}_4)_3$ respectively, substitution of Fe^{3+} for Al^{3+} reduces Fe^{3+} covalency (larger B value, Table 3). If $\text{Fe}^{3+}\text{-O}$ bonds are more covalent than $\text{Al}^{3+}\text{-O}$, net charge on the oxygens is reduced and the $\text{Fe}^{3+}\text{-O}$ bonds will be less covalent in andradite than in grossular. However, the more prominent of the ${}^4A_1{}^4E(G)$ levels in schorlomite,



and in a pink andradite of composition $\text{Ca}_3(\text{Fe}_{1.35}^{3+}\text{Ti}_{0.65}^{3+})\text{Si}_3\text{O}_{12}$, are also observed at $22,700\text{ cm}^{-1}$ (Manning & Harris 1970), and in view of the fact that ν_2 for garnets remains fairly constant (Table 3), it would seem that the effect of andradite composition on B is not very important. In schlorlomite, in particular, each Fe^{3+} has at least one next-nearest neighbour Al^{3+} in the tetrahedral Si sites. Significantly, the schlorlomite cell-size $\gg$ andradite cell-size.

For spessartine ($(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})\text{Al}_2\text{Si}_3\text{O}_{12}$), and grossular, the replacement of Ca^{2+} by $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})$ is not expected to materially affect the electronic distribution about the Fe^{3+} octahedra. $\text{Ca}^{2+}\text{-O}$ bonds are likely to be of low covalent character, while the $(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+})$ bonds, because of their great length ($\text{Mg-O} = 2.28\text{ Å}$ in pyrope) in comparison to the sum of the metal-oxygen radii ($\text{Fe}^{2+} + \text{O}^{2-} = 2.11\text{ Å}$; $\text{Mn}^{2+} + \text{O}^{2-} = 2.16\text{ Å}$), will also be of low covalency. In garnets, at least, $\text{Fe}^{3+}\text{-O}$ covalency seems to depend principally on bond distance.

The Fe^{3+} B -values increase in the order kyanite < idocrase < muscovite, which is the order of increasing ease of substitution of Fe^{3+} .

Burns & Strens (1967) have related the ease of substitution of Fe^{3+} to the size of the parent Al^{3+} site. The small Al^{3+} sites in kyanite are less easily stretched to accommodate the larger Fe^{3+} ions. The Fe^{3+} B -values for the garnets also follow increasing ease of Fe^{3+} substitution, hence within the group of three garnets and within the other group of three non-garnets, covalency increases with decreasing site size, but whether the relationship holds between the two groups cannot definitely be answered. In andradite, for example, Fe^{3+} is a principal constituent and yet the B -value is only slightly larger than that for kyanite. Unfortunately, Fe^{3+} -O distances in any of these minerals are not known. Nevertheless, there would seem to be an approximate relationship between the B -value and the size of the Fe^{3+} octahedron.

The Mn^{2+} B -values indicate that the Mn^{2+} -O bonds in most of the silicates studied here and by Keester & White (1966) are of similar covalency. It is likely that the B -values are less sensitive in Mn^{2+} than in Fe^{3+} to changes in bond length, so that comparisons between B and bond length are not worthwhile.

In many of the minerals reported here, the Mn^{2+} and Fe^{3+} ions can occupy two or more sites of different bond lengths. Also, many of the sites are of low symmetry, and in some cases assignments of the spectral bands may not be unambiguous. In garnets, however, Fe^{3+} is known to occur predominantly in the octahedral sites, and the absorption spectra are consistent with this (Manning 1967*b*). Furthermore, the octahedral sites in garnets are relatively undistorted (Abrahams & Geller 1958). In muscovite, also, the spectra are consistent with Fe^{3+} being in the Al^{3+} sites only (Manning 1969). The reasonable correlation between B and bond distance suggests that the bands in Fe^{3+} spectra, for the most part, have been assigned correctly.

The band at $\sim 27,000\text{ cm}^{-1}$ marking the field-independent transition ${}^6A_1 \rightarrow {}^4E(D)$ in Fe^{3+} is generally more intense than the band at $\sim 23,000\text{ cm}^{-1}$ marking transitions to the lower field-independent state. It is likely that the former transition is borrowing intensity from $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer transitions centred in the ultraviolet region, through mixing of charge-transfer states with d states. The degree of mixing depends on the energy difference, $E_{CT} - E_d$, thus explaining the greater enhancement of the $27,000\text{ cm}^{-1}$ band. Further, because charge-transfer bands are extremely broad, this mixing of states causes a broadening of the d - d band.

The Racah parameters measured here are of interest because they have been determined directly from the spectra. Jorgensen's (1966) values are based on the assumption that $C = 4B$, which relationship is shown not to be valid.

The B -value for Mn^{2+} in rhodonite determined in this work differs

from that of Keester & White (1966) because the latter did not resolve bands marking the transition ${}^6A_1 \rightarrow {}^4E(D)$, and assumed that this band was at the same energy as in tephroite and glaucocroite. In most of the Mn^{2+} spectra, the $d-d$ bands are sharp and the number of bands are compatible with Mn^{2+} being in one type of site only.

It is impractical at the present time to determine the contributions of σ -bonding and π -bonding to the overall covalency. Strong π -bonding is promoted by strong σ -bonding because charge build-up on the cation is then reduced. However, because of the small size and large formal charge on Fe^{3+} , π -bonding in most of the Fe^{3+} -bearing minerals is not likely to be important.

CONCLUSION

Racah parameters have been measured for Mn^{2+} and Fe^{3+} in a number of silicates. Because the B -parameters are a direct measure of the separations of the two lower field-independent states, they are useful in interpreting Fe^{3+} spectra. A qualitative relationship between B and the size of the Fe^{3+} octahedron is indicated. For garnets, B -values will also depend on composition of tetrahedral sites.

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