

INTENSITIES AND HALF-WIDTHS OF OCTAHEDRAL-Fe³⁺ CRYSTAL-FIELD BANDS AND RACAH PARAMETERS AS INDICATORS OF NEXT-NEAREST-NEIGHBOUR INTERACTIONS IN GARNETS

P. G. MANNING

Water Science Subdivision, Dept. of Environment, 562 Booth St., Ottawa, Ontario, K1A 0E7

ABSTRACT

Half-widths and extinction coefficients of bands marking crystal-field transitions ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ and Racah B -parameters have been collated for octahedral-Fe³⁺ ions in a series of natural and synthetic garnets. It is shown that these three parameters are reasonably consistent indicators of next-nearest neighbour substitution in garnets. In grossular and schorlomite, Si⁴⁺ ions are replaced by, respectively, more-covalently bonded ions, probably H⁺, and less-covalently bonded ions, Al³⁺ and Fe³⁺. The next-nearest neighbour composition in spessartine differs from that in almandine in that octahedral-Fe³⁺ ions in the former have 12 ionically-bonded Mn²⁺ in adjacent cube sites, whereas in almandine the adjacent cube sites contain a mixture of covalently-bonded Fe²⁺ ions and ionically-bonded Mn²⁺ ions. These results are consistent with chemical and infrared analyses.

INTRODUCTION

It was suggested recently (Manning 1973) that the intensities of Fe³⁺ crystal-field transi-

tions depend mainly on intensity-stealing from O²⁻ → Fe³⁺ UV-centred charge-transfer absorption, the intensity of which is related to the cation composition of the next-nearest neighbour (NNN) sites. Substitution of Si⁴⁺ ions by less-covalent Al³⁺ and Fe³⁺ causes a marked increase in intensity of the ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ transition in adjacent octahedral-Fe³⁺ ions. For example the extinction coefficient (ϵ) is 1 for Fe³⁺ in andradite, 24 in schorlomite and ~600 in gadolinium iron garnet. The Fe³⁺ band is broadened considerably in schorlomite (half-width = $\omega_{1/2}$ = 1300 cm⁻¹; Fig. 1) compared to andradite ($\omega_{1/2}$ = 600 cm⁻¹), probably for the reason that half of the Fe³⁺ ions have 2 non-Si NNN ions (Al³⁺ or Fe³⁺) and the other half one non-Si NNN. Hence, the crystal fields of the two Fe³⁺-centred octahedra are different and two spectra are superimposed. The $\omega_{1/2}$ -values for the transition ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ in octahedral-Fe³⁺ differ markedly from one garnet end-member to an-

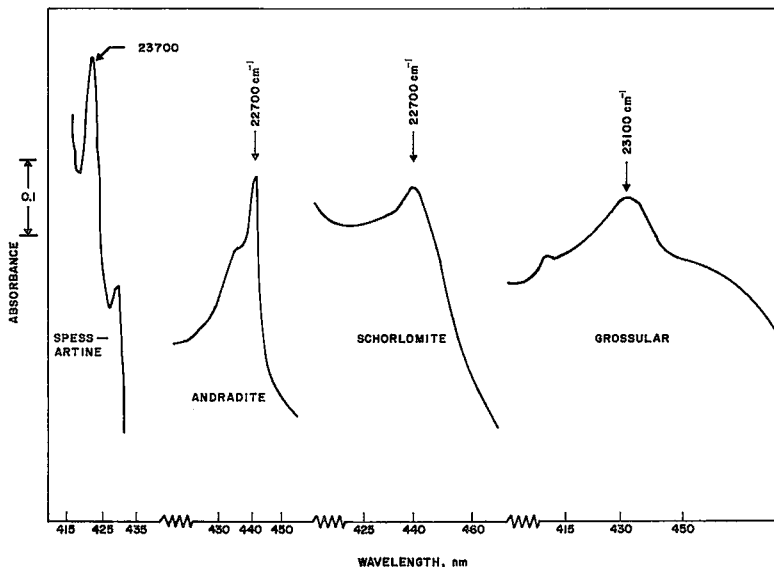


Fig. 1. Band profiles for the ${}^6A_1 \rightarrow {}^4A_1 {}^4E(G)$ transition in octahedral-Fe³⁺ ions in garnets. Note that transitions to the ${}^4A_1(G)$ and ${}^4E(G)$ levels are clearly distinguishable, and separated by ~ 400 cm⁻¹, in spectra of spessartine and andradite.

other (Moore & White 1972). Because octahedral sites in natural and synthetic garnets are regular (Abrahams & Geller 1958; Weidenborner 1961) it would appear that electronic distortions causing band broadening are a manifestation of NNN effects.

The Racah B -parameter is a measure of inter-electronic repulsion, the greater the degree of Fe^{3+} -oxygen covalency, the greater the degree of electron delocalization and the smaller is the value of B (Jorgensen 1962; Keester & White 1966; Manning 1970a). Not unexpectedly, B -values increase with increasing garnet cell-size and increasing Fe-O distance, thus $B = 500 \text{ cm}^{-1}$ for Fe^{3+} in spessartine, 557 cm^{-1} in grossular and 593 cm^{-1} in andradite (Manning 1970a). Substitution of Si by less-covalent Fe^{3+} and Al^{3+} ions increases electron density on the oxygens, leading to increased covalency of adjacent Fe^{3+} -oxygen bonds. It is anticipated that values of B will therefore decrease. The same mechanism promotes $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer absorption.

In this work, an attempt is made to determine whether the above parameters, B , $\omega_{1/2}$ and ϵ , are consistent in defining the nature of NNN interaction in natural garnets. The Fe^{3+} band used as an indicator marks the field-independent transition ${}^6A_1 \rightarrow {}^4A_1{}^4E(G)$.

EXPERIMENTAL DETAILS

All spectra, except that of a green grossular, have been reported earlier (Manning 1970a, 1969; Moore & White 1972; Slack & Chrenko 1971). The spectrum of the green grossular is a simple one of octahedral- Fe^{3+} ions, showing bands at the characteristic energies of 16800 cm^{-1} , 23100 cm^{-1} and 27000 cm^{-1} , marking transitions to the levels ${}^4T_2(G)$, ${}^4A_1{}^4E(G)$ and ${}^4E(D)$, respectively.

Extinction coefficients are calculated according to $\epsilon = A/Cl$ in litres/mole-cm, where A is net absorbance, C is Fe^{3+} concentration in moles/litre, and l is the crystal thickness in cm.

RESULTS AND DISCUSSION

A plot of B against garnet cell-size is presented in Figure 2. B is calculated as before (Manning 1970a) from the separation ($= 7B$) of the field-independent ${}^4A_1{}^4E(G)$ and ${}^4E(D)$ levels. The sharpness of bands marking transitions to these levels ($< 1000 \text{ cm}^{-1}$) serves to identify the transitions. Moore & White (1972) have assigned an absorption in almandine spectra at $\sim 23300 \text{ cm}^{-1}$, of half-width 1700 cm^{-1} (Manning 1972), to transitions to the ${}^4A_1{}^4E(G)$ levels. Because this band is considerably broader than the corresponding bands in spessartine ($\omega_{1/2} \sim 600 \text{ cm}^{-1}$)

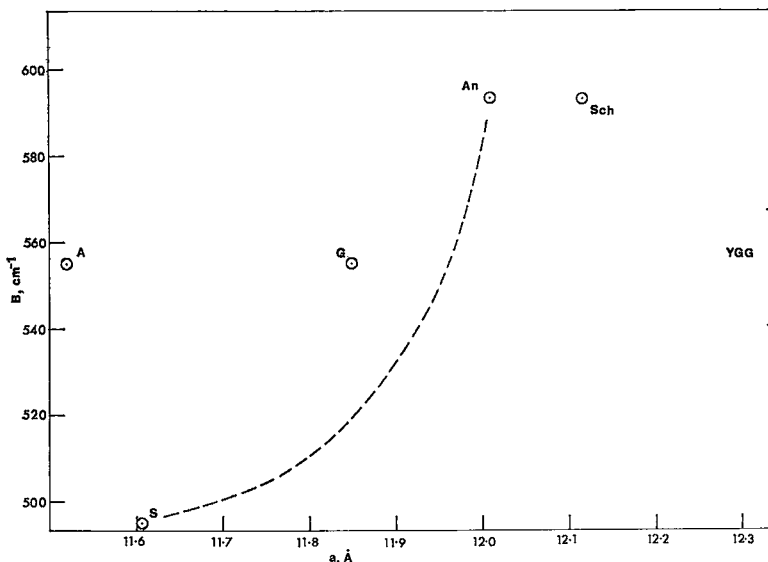


Fig. 2. A plot of B against a , the cell size, for octahedral- Fe^{3+} ions in garnets. Dotted line represents a curve based on all next-nearest neighbour tetrahedral ions being Si^{4+} , and adjacent cube sites containing ionically-bonded Ca^{2+} or Mn^{2+} . A = almandine, S = spessartine, G = grossular, An = andradite, Sch = schorlomite, YGG = yttrium gallium garnet.

and andradite ($\omega_{1/2} \sim 600 \text{ cm}^{-1}$), I made no assignment of the almandine feature. However in view of the fact that a band marking the transition ${}^6A_1 \rightarrow {}^4E(D)$ in octahedral- Fe^{3+} is seen at 27100 cm^{-1} , I feel that Moore & White's assignment is correct. This is supported by a recent observation of mine that the corresponding band in a spectrum of a green grossular has a half-width of 1400 cm^{-1} . Hence, for Fe^{3+} in almandine, $B = 1/7(27100 \text{ minus } \sim 23300) \approx 550 \text{ cm}^{-1}$. Half-widths and ϵ -values of Fe^{3+} bands in garnets are listed in Table 1.

The plot in Figure 2 shows no definite trend. The first obstacle in interpreting the plot is identifying those garnets in which all octahedral- Fe^{3+} ions are subjected to an identical crystal field, i.e. those in which the composition of the NNN sites is the same around all Fe^{3+} ions, and to use these as references for comparisons with other garnets. In these garnets, it is assumed, initially at least, that all NNN tetrahedral ions are Si^{4+} . Spectra of andradite and spessartine (Manning 1972) show two sharp absorption bands (overall $\omega_{1/2} \sim 600 \text{ cm}^{-1}$) corresponding to transitions to slightly separated ${}^4A_1(G)$ and ${}^4E(G)$ levels. In gadolinium iron garnet, the corresponding band is sharp ($\omega_{1/2} < 900 \text{ cm}^{-1}$, Levenson & Sawatsky 1969), and here we know that all NNN ions are cube- Gd^{3+} and tetrahedral- Fe^{3+} . I propose that in spessartine and andradite all octahedral- Fe^{3+} ions have 6Si^{4+} as NNN tetrahedral ions. If one NNN tetrahedral ion is Fe^{3+} or Al^{3+} , $\epsilon = 10$ (Manning 1973), hence $>90\%$ of octahedral- Fe^{3+} have 6Si^{4+} as NNN ions, otherwise a second set of absorption bands would be seen. Electron-microprobe analysis gave a molecular formula for one of the andradites studied of $\text{Ca}_{6.12}\text{Fe}_{9.95}^{3+}\text{Mn}_{0.03}\text{Si}_{5.96}\text{O}_{24}$, indicating insignificant substitution into Ca and Si sites. The ϵ -value of 1.5 for Fe^{3+} in andradite is consistent with all NNN tetrahedral ions being Si^{4+} .

The B -values for spessartine and andradite show that B increases with increasing cell-size.

TABLE 1. VALUES OF α , B , ω AND ϵ FOR OCTAHEDRAL- Fe^{3+} IONS IN GARNETS

Garnet	$\alpha(\text{\AA})$	B^{**}, cm^{-1}	$\omega_{1/2}, \text{cm}^{-1}$	ϵ
Almandine	11.525	550	1700	-
Spessartine	11.610	490	600	-
Grossular (green)	11.865	555	1400	1
Grossular (brown)	11.855	557	1000	1
Andradite	12.01	593	600	1.5
Schorlomite	12.13	~ 590	1300	24
Synthetic*	~ 12.3	~ 550	< 900	~ 600

*Synthetic garnets, yttrium gallium (Wood & Remeika 1967) or gadolinium iron garnets.

** B -values for octahedral- Fe^{3+} ions in several minerals are listed by Manning (1970a,b).

The B -value for octahedral- Fe^{3+} in yttrium gallium garnet ($\sim 550 \text{ cm}^{-1}$, Table 1) lies well below any reasonable curve joining the spessartine and andradite points. It is likely that the B -value for Fe^{3+} in schorlomite ($\approx B$ for andradite) is also lower than expected (Table 1, Fig. 2). These low values of B , as anticipated in the Introduction, reflect Si-substitutions by less-covalent ions, to the extent of 25% in schorlomite (Al^{3+} and Fe^{3+}) and 100% in synthetic garnets. Ferric ion B -values are likely more sensitive to Si-substitution than Ca^{2+} -substitution on account of the relatively low covalent character of Ca^{2+} -O bonds. The trends in B -values for Fe^{3+} in andradite, schorlomite and synthetic garnets are therefore consistent with the respective ϵ -values of 1.5, 24 and 600 in defining the NNN interaction as Si-substitution by less-covalent ions (Manning 1973). The schorlomite band is the broadest of the three because of the two different NNN environments.

The $\omega_{1/2}$ values for grossulars (Table 1) suggest NNN interaction, but the ϵ -value of 1 indicates Si-substitution by other covalent ions (Manning 1973), for example H^+ , but not by Fe^{3+} or Al^{3+} . Calculated B -values for octahedral- Fe^{3+} ions in vesuvianite ($B = 630 \text{ cm}^{-1}$) and muscovite ($B = 670 \text{ cm}^{-1}$), in which Fe^{3+} ions are bonded to one and two OH ions respectively, are significantly larger than for other Fe^{3+} -bearing minerals (Manning 1970a), even though the parent Al-O distances are similar to those in grossular (Abrahams & Geller 1958; Warren & Modell 1931; Radoslovich 1960). This suggests that O-H bonds are more covalent than O-Si and that the B -value for Fe^{3+} in grossular is inflated. That the point for grossular in Figure 2 lies close to a line joining spessartine and andradite must therefore be considered fortuitous. The point for grossular should then lie above a theoretical curve joining the spessartine and andradite points, representing 6Si^{4+} NNN tetrahedral ions and ionically-bonded NNN cube ions. The slope of the spessartine-andradite curve, marked by the dotted line in Figure 2, is therefore smaller at the smaller a -values, suggesting that the octahedral sites are too tight for efficient electron delocalization and covalent interaction. The solubility of Fe^{3+} ions in minerals having octahedral Al-O distances $< 1.92 \text{\AA}$ (Burns & Strens 1967) is low. The octahedral sites in pyrralspites are likely of these dimensions. Significantly, andradite, the Fe^{3+} -rich garnet, lies on the steeply-sloping portion of the curve, where degree of covalency is sensitive to Fe-O distance.

There is considerable evidence to support the presence of OH in grossular. The infrared spectra of grossulars reported by Slack & Chrenko (1971),

and confirmed by me, show strong OH absorption at 3600 cm^{-1} . Secondly, grossulars can be grown hydrothermally, and Yoder (1950) believes that most grossulars are in fact hydrogrossulars. Thirdly, hydrogrossulars in which $\sim 15\%$ of Si^{4+} ions are replaced by 4H^+ are well characterized (Deer, Howie & Zussman 1962). I propose that in grossulars, most octahedral- Fe^{3+} ions have one H^+ in adjacent "tetrahedral" sites (out of 6), with smaller amounts of Fe^{3+} having O and 2H^+ . I have placed the point for Fe^{3+} in grossular $\sim 40\text{ cm}^{-1}$ above the dotted line in Figure 2, corresponding to a difference in $7B$ of 280 cm^{-1} , which is considerably less than the half-widths of grossular bands (Table 1). A B -difference of 40 cm^{-1} seems reasonable in view of the relatively large B -values for Fe^{3+} in vesuvianite and muscovite.

The relatively large B - and $\omega_{1/2}$ -values for almandines (Table 1, Fig. 2), compared to spessartine, suggest NNN interaction. The large B -value precludes substitution of Si^{4+} ions by Al^{3+} and Fe^{3+} . Infrared spectra reported by Slack & Chrenko (1971), and confirmed by me, show little or no OH absorption. It would appear the NNN effects are related to compositional changes in the adjacent cube sites. I propose that Fe^{2+} -O bonds are more covalent than Mn^{2+} -O bonds, and that in spessartines, octahedral- Fe^{3+} ions have 12 ionically-bonded Mn^{2+} ions as NNNS. The large B - and $\omega_{1/2}$ for Fe^{3+} in almandines reflect a varied composition of covalently-bonded Fe^{2+} and ionically-bonded Mn^{2+} ions in adjacent cube sites. Electron-microprobe analysis of one of the spessartines examined spectrally gave 11% FeO and 32% MnO, corresponding to a $\text{Mn}^{2+}:\text{Fe}^{2+}$ ratio of $\sim 3:1$. The $\text{Mn}^{2+}:\text{Fe}^{2+}$ ratio in almandines is generally smaller than 1:10 (Deer, Howie & Zussman 1962). In pyral-spite garnets containing, say, $\sim 1\%$ or less Fe^{3+} , cation ordering in adjacent sites would seem to be extensive.

The current analysis of three octahedral- Fe^{3+} crystal-field parameters is of interest for many reasons.

(i) It demonstrates the principal covalent interactions in minerals. The relatively-high covalency of Si^{4+} -O and $\text{Al}^{3+}_{\text{VI}}$ -O bonds has been commented upon in an earlier work (Manning 1973), and to this group we can now add $\text{Fe}^{2+}_{\text{VI}}$ -O. The covalency of Si-O, $\text{Al}^{3+}_{\text{VI}}$ -O and $\text{Fe}^{2+}_{\text{VI}}$ -O bonds in almandines explains its resistance to weathering and use as an abrasive.

(ii) Information can be obtained on the nature of next-nearest neighbour substitutions, and also

on the ordering of NNN cations, e.g. spessartine and muscovite (Manning 1973).

(iii) Because octahedral- Fe^{3+} ions in almandines and spessartines appear to have 6Si^{4+} as NNN cube ions, $\epsilon \sim 1$.

(iv) Most importantly, the current work demonstrates that Fe^{3+} Racah B -parameters, spectral band half-widths and extinction coefficients can be consistent in defining the nature and origin of next-nearest interactions in silicates.

REFERENCES

- ABRAHAM, S.C. & GELLER, S. (1958): Refinement of the structure of a grossularite. *Acta Cryst.* **11**, 437-441.
- BURNS, R.G. & STRENS, R.G.J. (1967): Structural interpretations of polarized absorption spectra of epidotes. *Mineral. Mag.* **36**, 204-217.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals*, Vol. 1. Longman, Green & Co., London, p. 77.
- JORGENSEN, C.K. (1962): The nephelauxetic series. *Prog. Inorg. Chem.* **4**, John Wiley, New York, p. 73.
- KEESTER, K.L. & WHITE, W.B. (1966): Crystal-field spectra and chemical bonding in manganese minerals. Proc. 5th Int. Mineral Assoc. Meeting, Cambridge, U.K.
- LEVENSON, M. & SAWATSKY, E. (1969): Optical absorption in gadolinium iron garnet in the region 2000-5000Å. *J. Appl. Phys.* **40**, 2672-2673.
- MANNING, P.G. (1969): Optical absorption studies of grossular, andradite and uvarovite. *Can. Mineral.* **9**, 723-729.
- (1970a): Racah parameters and their relationship to lengths and covalencies of Mn^{2+} — and Fe^{3+} —oxygen bonds in silicates. *Can. Mineral.* **10**, 677-688.
- (1970b): Composition of garnets in interstellar dust. *Nature* **227**, 1121-1123.
- (1973): Extinction coefficients of Fe^{3+} spectral bands in oxides and silicates as indicators of local crystal composition. *Can. Mineral.* **12**, 120.
- MOORE, R.K. & WHITE, W.B. (1972): Electronic spectra of transition metal ions in silicate garnets. *Can. Mineral.* **11**, 791-811.
- RADOSLOVICH, E.W. (1960): The structure of muscovite. *Acta Cryst.* **13**, 919-932.
- SLACK, G.A. & CHRENKO, R.M. (1971): Optical absorption of natural garnets from 1000 to 30000 wavenumbers. *J. Opt. Soc. Amer.* **61**, 1325-1329.
- WARREN, B.E. & MODEL, D.I. (1931): The structure of vesuvianite. *Zeits. Krist.* **78**, 422-432.
- WEIDENBORNER, J.E. (1961): Least-squares refinement of the structure of gadolinium-iron garnet. *Acta Cryst.* **14**, 1051-1056.
- WOOD, D.L. & REMEIK, J.P. (1967): Effect of impurities on the optical properties of yttrium iron garnet. *J. Appl. Phys.* **38**, 1038-1045.

Manuscript received May 1973.