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A MÖSSBAUER SPECTRAL STUDY OF FERROUS AND FERRIC ION DISTRIBUTIONS IN GROSSULAR CRYSTALS: EVIDENCE FOR LOCAL CRYSTAL DISORDER

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ABSTRACT

A Mössbauer spectral study is reported of the distribution of ferrous and ferric ions in five grossular crystals that differ in composition. Measurements were conducted at room temperature. Ferrous ion absorptions were observed in four of the Mössbauer spectra, the calculated values of peak half-width (~0.25mms^{-1}), isomer shift and quadrupole splitting showing that ferrous ions are on one site, the 8-coordinate, only. Broad ferric absorptions, of half-width 0.38 to 0.59mms^{-1}, were observed in four of the Mössbauer spectra, the calculated values of isomer shift and quadrupole splitting showing that all ferric ions are on octahedral sites. The large half-widths reflect local disorder around ferric ions and this is attributed to replacement of SiO_4 by 4(OH) in next-nearest neighbor tetrahedral sites. Structural water analyses for four of the crystals gave values in the range 0.1 to 0.44% (by weight), and for three of the crystals, for which reliable half-widths were measured, the half-widths of the Fe^{3+} Mössbauer peaks increased with increasing $H_2O:Fe^{3+}$ ratio.

Previously published optical-absorption spectra of some grossular crystals are re-examined and an earlier suggestion that some of the optical bands are caused by tetrahedral-ferric ion is shown to be improbable. The ratio $Fe^{2+}:Fe^{3+}$ for the different grossular crystals ranges from 20:1 to less than 1:50.

SOMMAIRE

La distribution des ions ferreux et ferriques dans cinq cristaux de grossulaire de compositions différentes a été étudiée par spectroscopie Mössbauer; les mesures ont été faites à la température ordinaire. L'absorption d'ions ferreux est notée dans quatre des spectres Mössbauer; les valeurs calculées de la demi-largeur de pic (~0.25 mms^{-1}), du déplacement isomérique et du dédoublement quadripolaire indiquent que les ions ferreux sont tous en coordination 8. On observe de larges bandes d'absorption ferrique, dont la demi-largeur va de 0.38 à 0.59 mms^{-1}, dans quatre des spectres Mössbauer; les valeurs calculées du déplacement isomérique et du dédoublement quadripolaire placent tous les ions ferriques sur sites octaédriques. Les grandes demi-largeurs reflètent un désordre local autour des ions ferriques, désordre attribué au remplacement de Si^{4+} par $4H^+$ [SiO_4 par 4(OH)] dans les sites tétraédriques deuxièmes voisins. La détermination de l'eau structurale dans quatre des cristaux donne des valeurs allant de 0.1 à 0.44% (en poids); pour trois cristaux qui ont fourni de bonnes mesures des demi-largeurs, la demi-largeur des pics Fe^{3+} augmente avec le rapport H_2O/Fe^{3+}. Après ré-examen des spectres d'absorption optique de certains cristaux de grossulaire publiés précédemment, l'attribution de certaines des bandes optiques à l'ion ferrique tétraédrique s'avère improbable. Le rapport Fe^{2+}/Fe^{3+} dans les différents cristaux va de 20/1 à moins de 1/50.

(Traduit par la Rédaction)

INTRODUCTION

The field-independent transition $^6A_1 \rightarrow {}^4A_1{}^4E(G)$ in octahedrally-coordinated ferric ions is marked in optical-absorption spectra of spessartine and andradite garnets by two-component envelopes of half-width 500cm^{-1} at 300°K (Manning 1972; Moore & White 1972). The corresponding envelopes in spectra of schorlomites (centred at 22700cm^{-1}) and of grossulars (centred at 23100cm^{-1}) are considerably broader, having half-widths in the 1000cm^{-1} to 1400cm^{-1} range (Manning 1973). Band broadening in schorlomite spectra has been attributed to Si-Al-Fe^{3+} mixed-occupancy of next-nearest neighbor tetrahedral positions (Manning 1973) in which presumably random substitution gives rise to a variety of crystal fields around octahedral-ferric

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ions. Mössbauer spectra of schorlomites are complex, but appear to comprise two moderately broad doublets each of half-width 0.35mms^{-1}, marking ferric ions in octahedral and tetrahedral coordination (Burns 1972; Dowty 1971; Huggins *et al.* 1975). The broadening of the $^4A_1$ $^4E(G)$ optical bands in spectra of grossulars has been attributed to the replacement of SiO_4 by 4(OH) (Manning 1973), but it has also been suggested that the same grossular spectra contain broad absorptions of tetrahedral ferric ions at 19200cm^{-1} and at 21800cm^{-1} (Moore & White 1972). This article describes a Mössbauer spectral study of five grossular crystals so that the nature of the next-nearest neighbor interaction can be defined more clearly. Some previously published optical-absorption spectra of grossulars are re-examined.

EXPERIMENTAL DETAILS

Transmission Mössbauer spectra of powdered grossulars were measured by the method described in Manning & Tricker (1975). Experimental Mössbauer envelopes were fitted assuming the half-widths and the area ratios of each peak of a quadrupole doublet to be equal. X^2 tests and visual examination of the fits were used as criteria of goodness of fit. The line widths of the inner peaks of iron-foil spectra measured 0.25mms^{-1}.

Mr. H. G. Ansell, Geological Survey of Canada, Ottawa, and Dr. R. Gait, Royal Ontario Museum, Toronto, donated good crystallized specimens of grossular from the following localities: York River, Dungannon Township, Ontario; Ruberoid mine, Eden Mills, Vermont; Jeffrey mine, Asbestos, Quebec; and Mexico. Colors of the crystals were reddish brown, reddish brown, light brown, and green, respectively. Mr. Ansell also gave crystals of an andradite, from Stanley Peak, Arizona, and of a schorlomite from Magnet Cove, Arkansas. Mössbauer spectra of these garnets were run to give a better basis for interpreting the line-widths of the grossular bands. Electron microprobe analyses of the Dungannon, Eden Mills and Jeffrey mine grossulars were performed by Mr. D. Owens, CANMET, Ottawa. Analyses for structural water were performed by Mr. S. Abbey, Geological Survey of Canada, Ottawa. All analyses are listed in Table 1. All grossulars studied have unit-cell edges of 11.85Å to 11.86Å; these values were measured by Messrs. J. Stewart and E. Murray, CANMET.

TABLE 1. MICROPROBE ANALYSES OF GROSSULARS AND CALCULATED MOLECULAR FORMULAE

Wt.%	Ideal	Dungannon**	Eden Mills†	Jeffrey††	Mexico
FeO		4.9	3.7	1.4	2.0
TiO_2		0.3	0.0	0.4	
MnO		0.1	0.1	0.7	
SiO_2	40.02	39.2	39.6	38.7	
CaO	37.35	36.5	36.8	36.5	
Al_2O_3	22.63	19.6	20.9	21.7	
MgO		0.2	n.d.	n.d.	
Cr_2O_3		n.d.	n.d.	n.d.	
H_2O^+ (struct.)*		0.32	0.23	0.10	0.44
Total:	100.00	101.1	100.3	99.5	

n.d.=not detected (<0.01%)

* Determined by lead oxide fusion and titration with Karl Fischer reagent.

** Yields formula $(Ca_{5.94}Fe^{2+}_{0.18})(Al_{3.50}Fe^{3+}_{0.44}Ti_{0.06}Mn_{0.01}Mg_{0.05})Si_{5.98}(Si\equiv 4H)_{0.08}O_{24}$.

† Yields formula $(Ca_{5.90}Fe^{2+}_{0.25})(Al_{3.71}Fe^{3+}_{0.21}Mn_{0.01})Si_{5.87}(Si\equiv 4H)_{0.07}O_{24}$

†† Yields formula $(Ca_{5.94}Fe^{2+}_{0.17})(Al_{3.89}Fe^{3+}_{0.01}Mn_{0.09}Ti_{0.05})Si_{5.89}(Si\equiv 4H)_{0.02}O_{24}$

TABLE 2. MÖSSBAUER PARAMETERS (in mms^{-1}) AND $Fe^{2+}:Fe^{3+}$ VALUES FOR A SUITE OF IRON-BEARING GROSSULARS

Locality	FERROUS			FERRIC				
	HW	IS	QS	HW	IS	QS	$Fe^{2+}:Fe^{3+}$	$\%H_2O:Fe^{3+}$
Jeffrey	0.24	1.27	3.58	-	-	-	~20*	~1.5
Unknown	0.25	1.27	3.57	0.52	0.37	0.60	1.25	
Eden Mills	0.26	1.28	3.58	0.53	0.39	0.62	1.20	0.18
Dungannon	0.26	1.27	3.60	0.38	0.39	0.60	0.41	0.12
Mexico	-	-	-	0.59	0.39	0.60	<0.02	0.3
Andradite	-	-	-	0.27	0.39	0.60	<0.02	
Schorlomite				0.32	0.42	0.70	<0.02	
Almandine**	0.40	1.24	3.53					

All values relative to iron foil. Estimated errors in Mössbauer ±0.04 mms^{-1}.

* calculated assuming ferric parameters of HW 0.45, IS 0.39 and QS 0.60 mms^{-1}.

** adapted from Bancroft *et al.* (1967).

Oscillator strengths *(f)* are calculated from the expression $f=4.6\times10^{-9}\times$ (band half-width, in cm^{-1})$\times\epsilon$, where ϵ is the extinction coefficient, which is calculated, in turn, from net band absorbance divided by the product of cation concentration (in moles per litre) and sample thickness (in cm).

RESULTS AND DISCUSSION

The most complex of the Mössbauer spectra, those of the Dungannon and Eden Mills grossular crystals, are presented in Figures 1 and 2. These and the other grossular spectra were fitted satisfactorily with two doublets. Our calculated values of isomer shift (IS) and quadrupole splitting (QS) (Table 2) are in reasonable agreement with those measured earlier (Bancroft *et al.* 1967) for 8-coordinate Fe^{2+} in almandine and octahedrally-coordinated Fe^{3+} in andradite. The source used by Bancroft *et al.* gave a line-width of 0.35mms^{-1} with a sodium nitro-

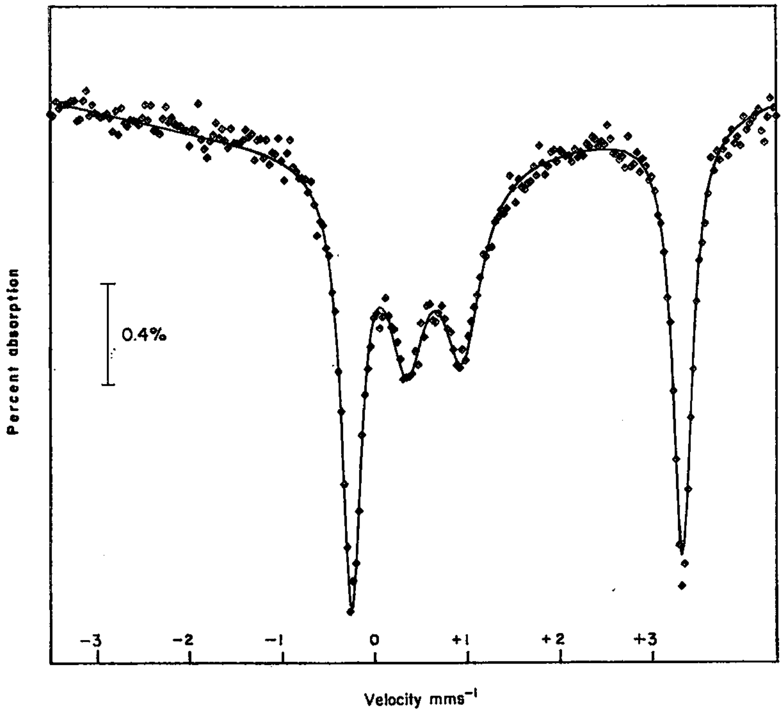

FIG. 1. Transmission Mössbauer spectrum of a powdered specimen of the Eden Mills grossular at 300°K. Continuous line represents computer-generated envelope. $X^2=210$ with 238 degrees of freedom. Total counts 2.25×10^6.

prusside absorber; our resolution is better than this, and for this reason we have measured the Mössbauer parameters for an andradite and for a schorlomite.

The half-widths of the ferrous doublets are approximately equal for all grossular crystals (Table 2), showing that as expected there is one type of 8-coordinate site in garnets. (The inner peaks of iron-foil spectra measured 0.25mms^{-1}). In contrast, half-widths of the ferric ion absorptions are considerably greater, and, too, differ significantly from one grossular crystal to another. This indicates a variety of next-nearest neighbor environments around octahedral–ferric ions. Supporting this, we measured half-widths of 0.27mms^{-1} for the ferric peaks in the Mössbauer spectrum of the Stanley Peak andradite and of 0.32mms^{-1} for the octahedral–ferric doublet in the spectrum of schorlomite. Significantly, the broadest Mössbauer (half-width 0.59mms^{-1}) and 23100cm^{-1} crystal-field (half-width 1400cm^{-1}) absorptions were observed in spectra of the same green Mexican grossular, and this crystal also contained the most water.

Figure 3 shows the optical-absorption spectrum of the Eden Mills grossular after subtraction of ultraviolet-centred background absorption and, too, the resolved components of the net envelope. Curve resolution on the Dupont Model 310 Resolver is highly subjective, but the presence of all resolved bands is confirmed by obvious peaks and shoulders in the original spectrum (Manning 1969a). A weak shoulder at 24500cm^{-1} is probably caused by cube-Mn^{2+}. Moore & White (1972) list the same absorptions. The 16900cm^{-1} and 23100cm^{-1} bands mark transitions to the $^4T_2(G)$ and $^4A_1{}^4E(G)$ levels in octahedral–ferric ions, but the origin of the 19000cm^{-1} and 21700cm^{-1} bands is in dispute. Moore & White (1972) assign the 19000cm^{-1} and 21700cm^{-1} bands to transitions to the $^4T_2(G)$ and $^4A_1{}^4E(G)$ levels in tetrahedral Fe^{3+}. The half-width of the latter band (2700cm^{-1}) seems too large for a field-independent transition, even allowing for next-nearest neighbor interaction. Attempts to fit the Eden Mills and Dungannon Mössbauer spectra by introducing a third doublet with parameters (IS and QS) characteristic of tetrahedral–ferric ions (e.g. Burns 1972) were unsuccessful. We estimate that not more than 2% of total Fe in these grossulars is tetrahedral ferric. The oscillator strength of the 23100cm^{-1} band, calculated from information in Figure 3 and Tables 1 and

2, is 4×10^{-6}, whereas the value for the 21700cm^{-1} band, on the basis that it is caused by tetrahedral–ferric ion, is not less than 2.5×10^{-4}. This f-value seems too large for a spin-forbidden transition, and suggests, in line with half-width considerations, that the 19000cm^{-1} and 21700cm^{-1} bands do not mark tetrahedral Fe^{3+}.

The 21700cm^{-1} and 19000cm^{-1} optical bands contribute in large measure to the reddish brown colors of the Dungannon and Eden Mills grossular crystals. These bands are in no way reminiscent of the complex absorptions of ferrous ions in visible-region spectra of garnets. They may mark Mn^{3+} ions on octahedral positions; similar bands are seen in the optical spectra of pink tourmalines at ~15000cm^{-1} and 19200cm^{-1} (Manning 1969b). The Mn^{2+}:Mn^{3+} ratio in our grossulars is not known, hence ϵ-values cannot be calculated. However, assuming that all the Mn in the Eden Mills and Dungannon grossular crystals is present as Mn^{3+}, ϵ ~40. Weak shoulders at ~24500cm^{-1} do suggest that some of the Mn is in the form of Mn^{2+}. The 21700cm^{-1} and 19000cm^{-1} bands are not observed in spectra of the green Mexican grossular, in which the 23100cm^{-1} band has its greatest half-width. If the broadening of the 23100 cm^{-1} band does arise from cation replacement in tetrahedral positions (by Al^{3+}, Fe^{3+}, H^{+}), then it would appear that the 21700cm^{-1} and 19000cm^{-1} bands are not caused by a tetrahedrally–bonded cation (e.g. Fe^{3+}).

Considering the data presented in Tables 1 and 2, it can be seen that, for the Dungannon, Eden Mills and Mexico grossular crystals, the 23100cm^{-1} band half-width increases with increasing H_2O:Fe^{3+} concentration ratios. Additionally, the presence of strong OH absorption at 3600cm^{-1} in infrared spectra of grossulars (Slack & Chrenko 1971; Manning 1973), the synthesis of hydrogrossulars from close to the grossular composition to $3CaO.Al_2O_3.6H_2O$ (Flint *et al.* 1941), and the well-characterized nature of hydrogrossulars (Deer, Howie & Zussman 1962), all support the contention that the principal replacement is SiO_4 by 4(OH). The half-widths of the grossular optical and Mössbauer absorptions are, in many cases, twice as large as the corresponding absorptions in andradite spectra, indicating that a high proportion of octahedral-ferric ions have next-nearest neighbor site compositions of $5Si+1H^{+}$ and $4Si+2H^{+}$. In the Dungannon material, ~1% of the tetrahedral

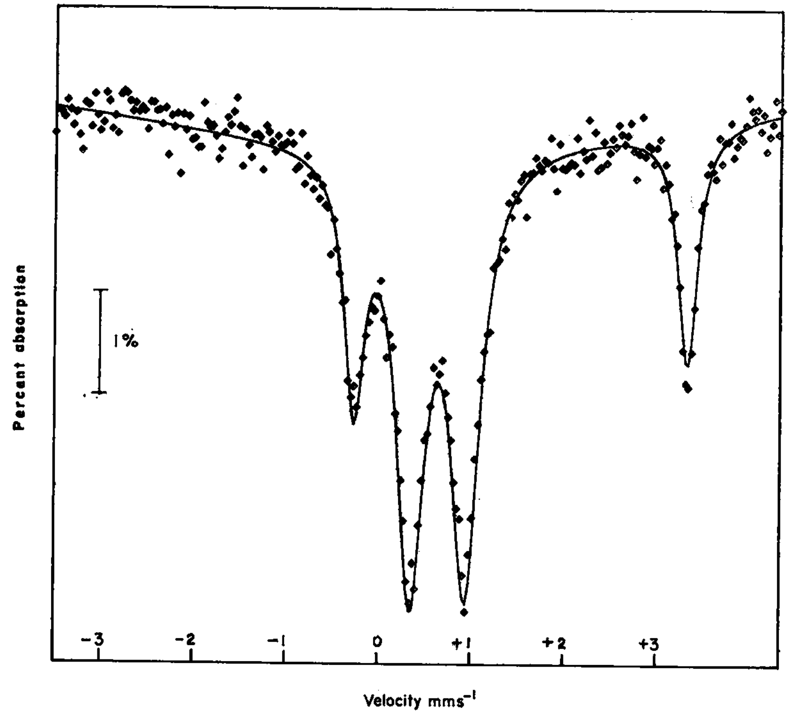

FIG. 2. Transmission Mössbauer spectrum of a powdered specimen of the Dungannon grossular at 300°K. Continuous line represents computer-generated envelope. $X^2=240$ with 238 degrees of freedom. Total counts 0.27×10^{6}.

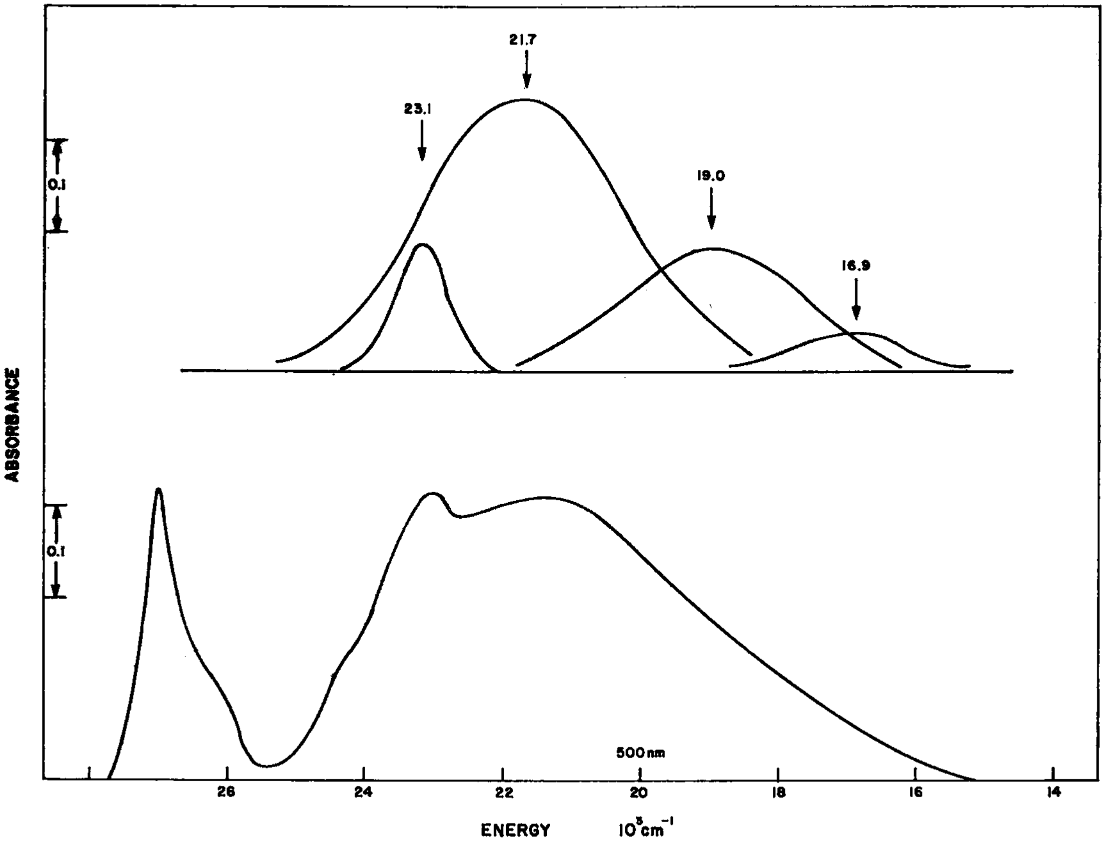

FIG. 3. Optical-absorption spectrum of the Eden Mills grossular after subtraction of an estimated ultraviolet-centred background (lower) and the resolved components (upper). Sample thickness 0.16cm.

positions are occupied by $4H^+$, which is equivalent to a concentration of 0.23 moles per litre Si. The total octahedral-ferric concentration is 1.74 moles per litre, a large fraction of which represents ferric ions with H^+ in a next-nearest neighbor tetrahedral position. It would appear, therefore, that ferric ions prefer the octahedral positions adjacent to the tetrahedral "holes". Each "hole" may fix four ferric ions on adjacent octahedral sites. If the ferric substitutions were random, the Si deficiency would have to be close to that in schorlomite, in which up to 25% of the tetrahedral sites are Si-deficient (Howie & Wooley 1968).

The ferrous absorptions in the Mössbauer spectra of grossulars are not broadened, indicating that either the Mössbauer parameters are not sensitive to different next-nearest neighbor compositions or that cube-ferrous ions have a statistical number of H^+ in adjacent tetrahedral sites. This number is sufficiently low that it would not lead to appreciable broadening of the ferrous bands.

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REFERENCES

BANCROFT, G. M., MADDOCK, A. G. & BURNS, R. G. (1967): Application of the Mössbauer effect to silicate mineralogy. *Geochim. Cosmochim. Acta* 31, 2219-2246.

BURNS, R. G. (1972): Mixed-valencies and site occupancies of iron in silicate minerals from Mössbauer spectroscopy. *Can. J. Spectros.* 17, 51-59.

DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1962): *Rock-Forming Minerals* 1, Longman, Green & Co., London.

DOWTY, E. (1971): Crystal-chemistry of titanian garnets. *Amer. Mineral.* **56**, 1983-2010.

FLINT, E. P., MCMURDIE, H. P. & WELLS, L. S. (1941): Hydrothermal and X-ray studies of the garnet-hydrogarnet series. *J. Res. U.S. Bur. Standards* **26**, 13-53.

HOWIE, R. A. & WOOLEY, A. R. (1968): The role of titanium and the effect of TiO_2 on the cell-size, refractive index, and specific gravity in the andradite-melanite-schorlomite series. *Mineral. Mag.* **36**, 775.

HUGGINS, F. E., VIRGO, D., HOLZL, E. & HUCKENHOLZ, H. G. (1975): Distribution of Al, Fe^{3+}, and Ti^{4+} between the octahedral and tetrahedral sites in garnets between $Ca_3Al_2Si_3O_{12}$ and $Ca_3Fe_2Ti_{1.416}Si_{1.584}O_{12}$. *Ann. Rep. Director Geophys. Lab., Carnegie Inst. Wash.*, 582.

MANNING, P. G. (1969a): Optical-absorption studies of grossular, andradite (var. colophonite) and uvarovite. *Can. Mineral.* **9**, 723-729.

——— (1969b): An optical-absorption study of the origin of colour and pleochroism in pink and brown tourmalines. *Can. Mineral.* **9**. 678-690.

——— (1972): Optical-absorption spectra of Fe^{3+} in octahedral and tetrahedral sites in natural garnets. *Can. Mineral.* **11**, 826-839.

——— (1973): Intensities and half-widths of octahedral-Fe^{3+} crystal-field bands and Racah parameters as indicators of next-nearest neighbour interactions in garnets. *Can. Mineral.* **12**, 215-218.

——— & TRICKER, M. J. (1975): Optical-absorption and Mössbauer spectral studies of iron and titanium site populations in vesuvianites. *Can. Mineral.* **13**, 259-265.

MOORE, R. K. & WHITE, W. B. (1972): Electronic spectra of transition-metal ions in silicate garnets. *Can. Mineral.* **11**, 791-811.

SLACK, G. A. & CHRENKO, R. M. (1971): Optical absorption of natural garnets from 1000 to 30000 wavenumbers. *J. Opt. Soc. Amer.* **61**, 1325-1329.

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