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 (~0.25 mms⁻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 0.59 mms⁻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 SiO₄ 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⁺⁺ Mössbauer peaks increased with increasing H₂O:Fe³⁺ 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⁺⁺:Fe³⁺ for the different grossular crystals ranges from 20:1 to less than 1:50.

INTRODUCTION

The field-independent transition ⁶A₁ → ⁴A₁'E(G) in octahedrally-coordinated ferric ions is marked in optical-absorption spectra of spessartine and andradite garnets by two-component envelopes of half-width 500 cm⁻¹ at 300 K (Manning 1972; Moore & White 1972). The corresponding envelopes in spectra of schorlomites (centred at 22700 cm⁻¹) and of grossulars (centred at 23100 cm⁻¹) are considerably broader, having half-widths in the 1000 cm⁻¹ to 1400 cm⁻¹ range (Manning 1973). Band broadening in schorlomite spectra has been attributed to Si-Al-Fe⁺⁺ 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.
ions. Mössbauer spectra of schorlomites are complex, but appear to comprise two moderately broad doublets each of half-width 0.35 mms⁻¹, marking ferric ions in octahedral and tetrahedral coordination (Burns 1972; Dowty 1971; Huggins et al. 1975). The broadening of the *A₁, E(G) optical bands in spectra of grossulars has been attributed to the replacement of SiO₄ by 4(OH) (Manning 1973), but it has also been suggested that the same grossular spectra contain broad absorptions of tetrahedral ferric ions at 19200 cm⁻¹ and at 21800 cm⁻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. χ² 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 0.25 mms⁻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. Abbe, Geological Survey of Canada, Ottawa. All analyses are listed in Table 1.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Ferrous</th>
<th>FERRIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HW</td>
<td>IS</td>
</tr>
<tr>
<td>Jeffrey</td>
<td>0.24</td>
<td>1.27</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.25</td>
<td>1.27</td>
</tr>
<tr>
<td>Eden Mills</td>
<td>0.26</td>
<td>1.26</td>
</tr>
<tr>
<td>Dungannon</td>
<td>0.26</td>
<td>1.27</td>
</tr>
<tr>
<td>Mexico</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Andradite</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Schorlomite</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Almandine**</td>
<td>0.30</td>
<td>1.24</td>
</tr>
</tbody>
</table>

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=4.6×10⁴×(band half-width, in cm⁻¹)×ε, 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 Fe³⁺ in almandine and octahedrally-coordinated Fe³⁺ in andradite. The source used by Bancroft et al. gave a line-width of 0.35 mms⁻¹ with a sodium nitro-
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 0.25 m/s). 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 0.27 m/s for the ferric peaks in the Mössbauer spectrum of the Stanley Peak andradite and of 0.32 m/s for the octahedral-ferric doublet in the spectrum of schorlomite. Significantly, the broadest Mössbauer (half-width 0.59 m/s) and 23100 cm⁻¹ crystal-field (half-width 1400 cm⁻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 24500 cm⁻¹ is probably caused by cube-Mn⁺. Moore & White (1972) list the same absorptions. The 16900 cm⁻¹ and 23100 cm⁻¹ bands mark transitions to the ²Tₗ₂(G) and ⁴A₁ₑ(G) levels in octahedral-ferric ions, but the origin of the 19000 cm⁻¹ and 21700 cm⁻¹ bands is in dispute. Moore & White (1972) assign the 19000 cm⁻¹ and 21700 cm⁻¹ bands to transitions to the ²Tₗ₂(G) and ⁴A₃ₑ(G) levels in tetrahedral Fe³⁺. The half-width of the latter band (2700 cm⁻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 23100 cm⁻¹ band, calculated from information in Figure 3 and Tables 1 and
2, is $4 \times 10^4$, whereas the value for the
21700 cm$^{-1}$ band, on the basis that it is caused
by tetrahedral-ferric ion, is not less than $2.5 \times
10^4$. This $f$-value seems too large for a spin-
forbidden transition, and suggests, in line with
half-width considerations, that the 19000 cm$^{-1}$
and 21700 cm$^{-1}$ bands do not mark tetrahedral
Fe$^{3+}$.

The 21700 cm$^{-1}$ and 19000 cm$^{-1}$ optical bands
contribute in large measure to the reddish brown
colors of the Dungannon and Eden Mills gross-
sular crystals. These bands are in no way re-
miniscent 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 $\sim$15000 cm$^{-1}$ and 19200 cm$^{-1}$
(Manning 1969b). The Mn$^{3+}$:Mn$^{2+}$ ratio in our
grossulars is not known, hence $\epsilon$-values cannot
be calculated. However, assuming that all the
Mn in the Eden Mills and Dungannon grossular
crystals is present as Mn$^{3+}$, $\epsilon \sim 40$. Weak
shoulders at $\sim$24500 cm$^{-1}$ do suggest that some
of the Mn is in the form of Mn$^{2+}$. The
21700 cm$^{-1}$ and 19000 cm$^{-1}$ bands are not ob-
served in spectra of the green Mexican grossu-
lar, in which the 23100 cm$^{-1}$ band has its great-
est 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 21700 cm$^{-1}$ and
19000 cm$^{-1}$ bands are not caused by a tetrahe-
drally-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
23100 cm$^{-1}$ band half-width increases with in-
creasing $\text{H}_2\text{O}:\text{Fe}^{3+}$ concentration ratios. Addi-
tionally, the presence of strong OH absorption
at 3600 cm$^{-1}$ in infrared spectra of grossulars
(Slack & Chrenko 1971; Manning 1973), the
synthesis of hydrogrossulars from close to the
grossular composition to $3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}$
(Flint et al. 1941), and the well-characterized
nature of hydrogrossulars (Deer, Howie & Zuss-
man 1962), all support the contention that the
principal replacement is SiOr by 4(OH). The half-
widths of the grossular optical and M"ossbauer ab-
sorptions are, in many cases, twice as large as the
corresponding absorptions in andradite spectra,
indicating that a high proportion of octahedral-
ferric ions have nearest-neighbor site com-
positions of 5Si$^1$H$^+$ and 4Si$^2$H$^+$. In the
Dungannon material, $\sim 1\%$ of the tetrahedral

![Fig. 2. Transmission M"ossbauer 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
$0.27 \times 10^9$.](image-url)
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.

ACKNOWLEDGEMENT

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REFERENCES


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