in the nepheline syenites of this area is noteworthy, as it has not been reported from anywhere else. This intergrowth may be the result of post-magmatic replacement.

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OPTICAL ABSORPTION STUDIES OF GROSSULAR, ANDRADITE (VAR. COLOPHONITE) AND UVAROVITE

P. G. MANNING*

In this note are reported the optical absorption spectra of an andradite (var. colophonite), two grossulars and an uvarovite. The purpose of the work is the identification of the band marking electronic transitions to the second field-independent state in octahedrally-bonded Fe^{3+}, i.e., the $^6A \rightarrow {}^4E(D)$ transition in Fig. 1.

A very sharp band in andradite spectra at 22,700 cm^{-1} has earlier been assigned to transitions to the first field-independent state (Fig. 1) in Fe^{3+} (Manning, 1967; Grum-Grzhimailo *et al.*, 1963). The same band is observed in the colophonite spectrum (Fig. 2) at 22,700 cm^{-1} and also in the spectra of the two grossulars at 22,800 cm^{-1} (Figs. 3 and 4). The spectra of the

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*Research Scientist, Mineral Sciences Division, Department of Energy, Mines and Resources, Ottawa, Canada.

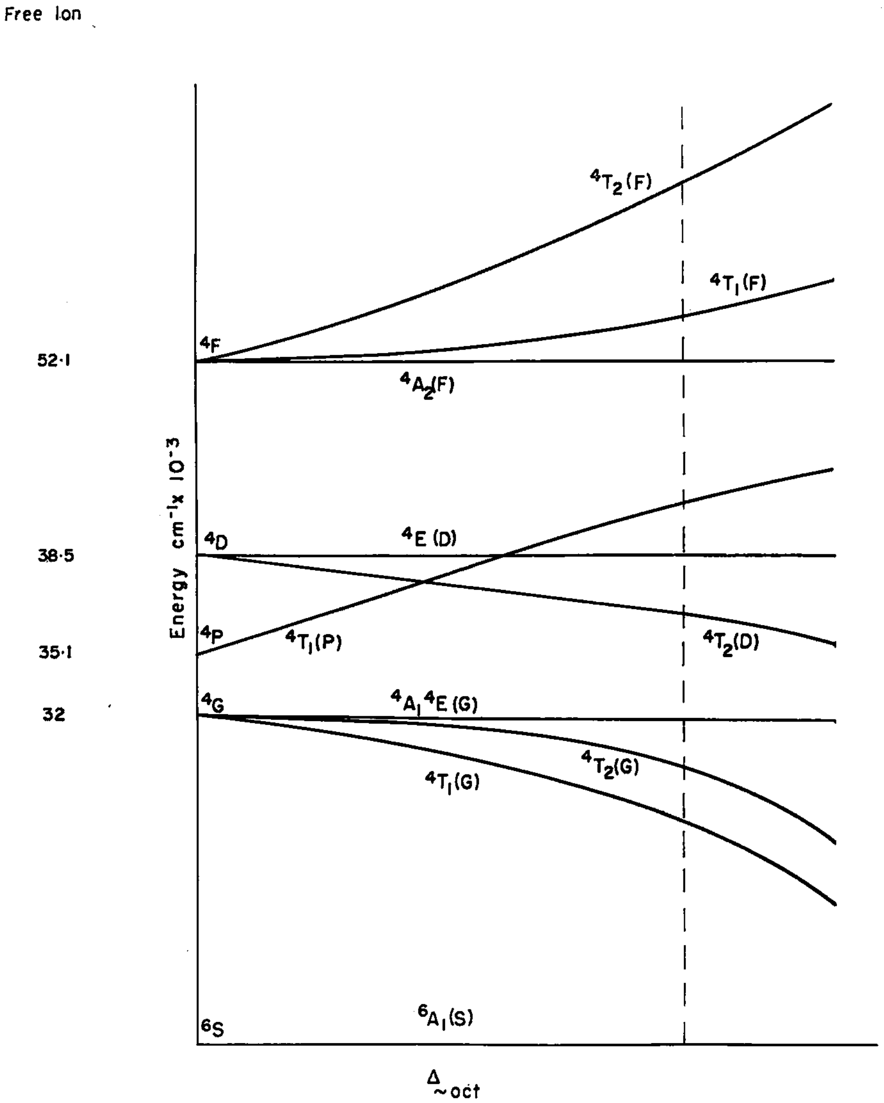

FIG. 1. Energy level diagram for Fe^{3+} in cubic fields.

grossulars are significantly different from the grossular spectra reported by Grum-Grzhimailo *et al.* (1954). The grossulars used in the current work were checked by *x*-ray to show that they were indeed grossulars.

Chemical analyses of the garnets studied are listed in Table 1. In general, the garnets are low in Ti and Mn. The grossular showed weak

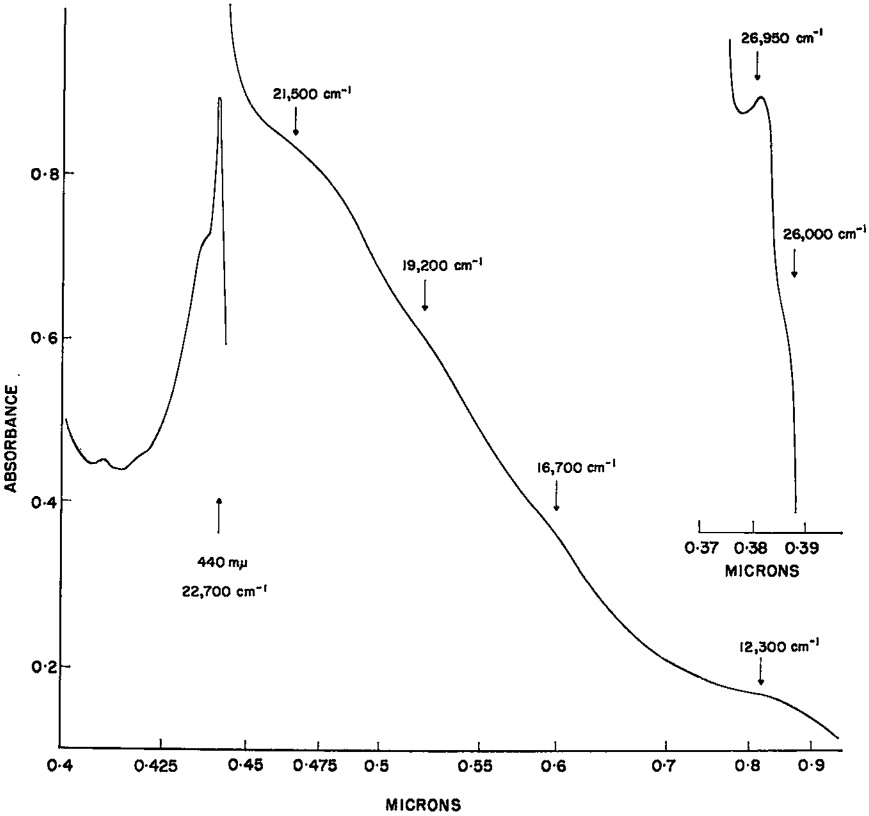

FIG. 2. Spectrum of andradite (var. colophonite) from Willsboro County, N.Y. Thickness = 0.32 mm.

8-coordinate Fe^{2+} bands in the infrared at 8,200 cm^{-1} and 5,700 cm^{-1}, corresponding to 1% Fe^{2+}, if $\epsilon = 1$ litre/mole-cm, for the York River grossular. The extinction coefficient, ϵ, is defined in the usual manner, and the value $\epsilon = 1$ has been taken from an earlier work (Manning, 1967b).

The uvarovite spectrum (Fig. 5) shows the two strong octahedrally-bonded Cr^{3+} bands at 16,600 cm^{-1} and 23,100 cm^{-1}. These bands are attributed to the spin-allowed transitions in Cr^{3+}, ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$ respectively (Fig. 6). Two Cr^{3+} bands have been observed in the spectra of blood-red pyrope (Manning, 1967) at 17,800 cm^{-1} and 24,100 cm^{-1}. For octahedrally-bonded Cr^{3+}, $\Delta E({}^4T_2 - {}^4A_2) = 10\ Dq$, where $10\ Dq$ is the splitting of e_g and t_{2g} orbitals. The larger splitting in pyrope reflects the shorter Cr^{3+}-O distances in pyralspites than in ugrandites (Abrahams & Geller, 1958; Zemann & Zemann, 1961).

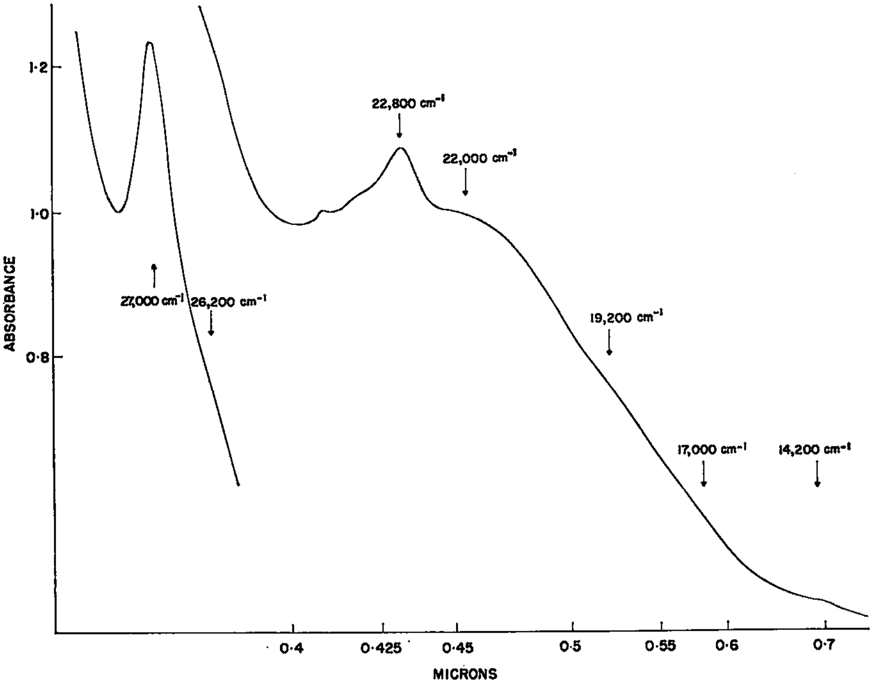

FIG. 3. Absorption spectrum grossularite from York River, Ontario. Thickness = 0.9 mm.

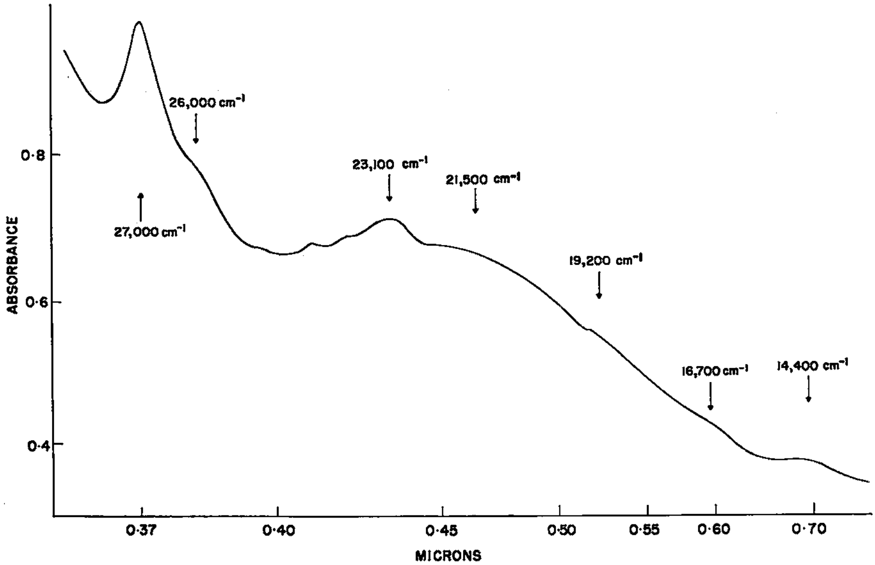

FIG. 4. Absorption spectrum of grossular from Ruberoid Mine, Vermont.

TABLE 1. CONCENTRATIONS OF CATIONS IN GARNETS IN WT. %

Cation	Andradite (Colophonite) Willsboro	Grossular York River	Grossularite Ruberoid	Uvarovite Thetford
Fe	16.8	3.39	1.5	2.2
Mn	0.2		0.20	
Ti	0.07	0.19	0.03	
Cr				10

The spectra of all garnets studied here show a relatively prominent and sharp absorption at ~27,000 cm^{-1}. The sharpness of the band suggests it marks transitions to the second field-independent state, $^4E(D)$, in octahedrally-bonded Fe^{3+}. All spectra also show a shoulder at ~26,000 cm^{-1} that can very reasonably be assigned to the transition $^6A_1 \rightarrow T_2(D)$. The 22,700 cm^{-1} band that would mark the first field-independent state in uvarovite is probably "swamped" by the strong 23,100 cm^{-1} Cr^{3+} band.

The distinctive nature of the 27,000 cm^{-1} band in ugrandites suggests it could be used for Fe^{3+} analyses, provided sufficient chemical analyses were available to obtain a reliable value for ϵ. An approximate value of ϵ taken from Figs. 2–4 is 2.

Absorption bands below 22,700 cm^{-1} are not well resolved in the andradite and grossular spectra (Figs. 2–4). Bands at ~21,500 cm^{-1} and

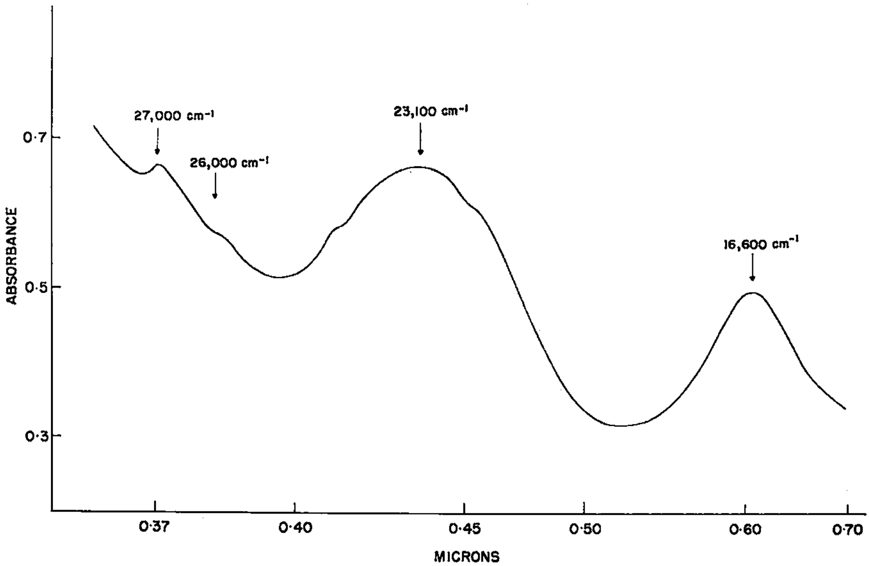

FIG. 5. Absorption spectrum of uvarovite from Thetford, Quebec. Thickness = 0.03 mm.

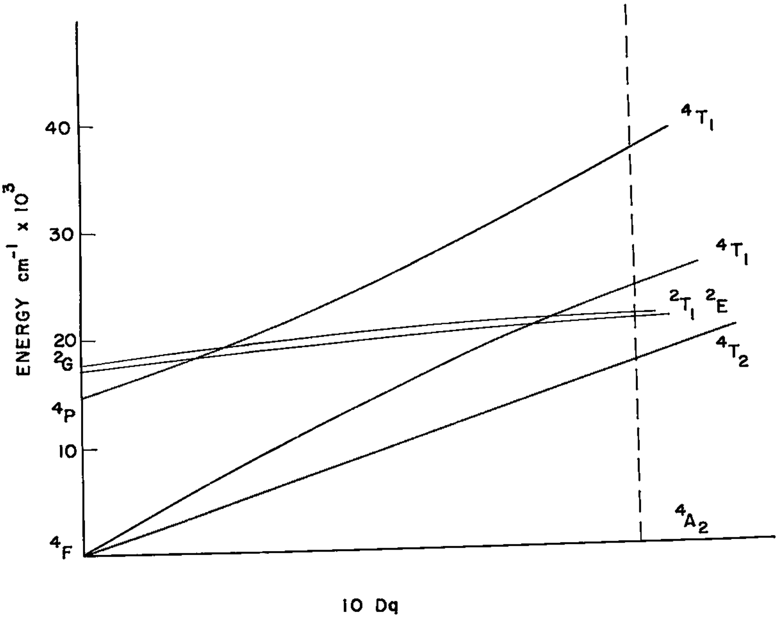

FIG. 6. Energy level diagram for Cr^{3+} in octahedral fields. Dotted line gives approximate 10 *Dq* for $Cr(OH_2)_6{}^{3+}$.

~12,000 cm^{-1} are readily evident in all three spectra while the colophonite spectrum (Fig. 2) shows weakly-resolved shoulders at ~16,700 cm^{-1} and ~19,200 cm^{-1}. These bands could be assigned in the following manner to Fe^{3+}:

$$\left.\begin{array}{l}\sim 12{,}000\ \text{cm}^{-1}\\ \sim 16{,}700\ \text{cm}^{-1}\end{array}\right\}\ {}^6A_1 \rightarrow {}^4T_1(G)$$

and

$$\left.\begin{array}{l}\sim 19{,}200\ \text{cm}^{-1}\\ \sim 21{,}500\ \text{cm}^{-1}\end{array}\right\}\ {}^6A_1 \rightarrow {}^4T_2(G)$$

The electronic configurations of the $^4T_1(G)$ and $^4T_2(G)$ levels are $t_{2g}^4e_g^1$, so that a dynamic Jahn–Teller mechanism could lead to a splitting of the bands. The assignments of these bands must be considered tentative.

Note added in proof:—

The absorption spectrum of a green muscovite from Villeneuve, P.Q., that contained 6% Fe^{3+}, showed well-resolved bands at the following energies:— 11,000 cm^{-1}; 16,600 cm^{-1}; 22,600 cm^{-1} (sharp); 26,000 cm^{-1} and 27,000 cm^{-1} (sharp). The assignments of these bands seem straightforward:—

$^6A_1 \rightarrow {}^4T_1(G)$	11,000 cm^{-1}
$^6A_1 \rightarrow {}^4T_2(G)$	16,600 cm^{-1}

$$
\begin{aligned}
& {}^6A_1 \rightarrow {}^4A_1{}^4E(G) && 22{,}600 \text{ cm}^{-1} \\
& {}^6A_1 \rightarrow {}^4T_2(D) && 26{,}000 \text{ cm}^{-1} \\
\text{and} \quad & {}^6A_1 \rightarrow {}^4E(D) && 27{,}000 \text{ cm}^{-1}.
\end{aligned}
$$

At the higher energies, the spectra of Fe^{3+} in muscovite and garnet are very similar.

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SULPHIDE RESEARCH CONTRIBUTIONS FROM THE MINERAL SCIENCES DIVISION, MINES BRANCH, DEPARTMENT OF ENERGY, MINES AND RESOURCES

E. H. NICKEL

Head, Mineralogy Section, Mineral Sciences Division, Mines Branch, Ottawa, Ontario

Several years ago it was decided that a significant proportion of the research activity of the scientific personnel of the Mineral Sciences Division should be directed toward a study of the properties and behaviour of sulphides and related minerals. This decision was based on the fact that sulphides represent an extremely important part of Canada's mineral economy and that the knowledge about the fundamental properties of sulphides and their genesis in nature is far from complete. Furthermore, it is generally recognized that advances in technology, in this case the recovery of sulphides from ore and their subsequent utilization, are ultimately predicated on increasing the reservoir of fundamental knowledge. The sulphide research programme, as it was conceived and put into practice, is a broadly inter-disciplinary one, with contributions being made by scientific personnel with a wide range of specialties.