# ON THE PLEOCHROISM OF VANADIUM-BEARING ZOISITE FROM TANZANIA

G. H. FAYE AND E. H. NICKEL *

## Abstract

A study of the polarized optical absorption spectra of both blue and tan-coloured, vanadium-bearing zoisite specimens from Tanzania, revealed a number of spectral features between 13,400 and 27,000 cm$^{-1}$. Most of these are attributed to V$^{3+}$ substituting on the Al$_3$ site of zoisite and are responsible for the dichroic scheme of the blue (heated) variety of zoisite (*i.e.* $E // Y \simeq E // Z$ (blue), $E // X$ (violet) ). An additional band at 22,500 cm$^{-1}$, thought to be due to Ti$^{3+}$, or V$^{4+}$, occurs in the $E // Z$ spectrum (yellow-green) of tan zoisite, thus producing a trichroic scheme.

Recently gemmologists have shown considerable interest in vanadium-bearing zoisite from Tanzania (Anderson 1968; Liddicoat & Crowningshield 1968; Meen 1968), the crystallographic, optical and physical properties of which have been described recently by Hurlbut (1969).

The most striking property of this material is its pleochroism which changes from trichroic to dichroic on heating. Although several of the principal absorption bands have been located with a spectroscope (Anderson 1968), the details of the absorption spectrum for each principal optical direction do not seem to have been reported. Only through a knowledge of the polarization properties of the spectral features can the pleochroism of the untreated and heated zoisite be understood. This note is devoted to that end.

A number of specimens of the Tanzanian zoisite were obtained through the courtesy of H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada. Of the two specimens (each conchoidally fractured), whose detailed spectra are reported in this study, one was tan in colour in ordinary white light and trichroic in polarized light, while the other was blue in white light, and dichroic in polarized light. Microprobe analysis gave for the tan crystal : V-0.26%, Ti-0.04%, Fe and Mn not detected; and for the blue crystal V-0.18%, Fe, Mn and Ti not detected. Microprobe analysis of two other specimens of the trichroic variety of zoisite showed their V contents to be 0.24 to 0.30%, and their Ti content to be 0.024%. The V and Ti contents of a second blue crystal were 0.20% and $<$ 0.01% respectively. Thus,

---

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

there is an apparent correlation between certain spectral properties of the Tanzanian zoisite and its titanium content.

Using an iterative procedure of cutting with a wire saw, and orienting by means of optical interference figures, rational sections were obtained from the tan crystal. After polishing, these sections were used to measure the polarized absorption spectra shown in Figure 1. The unpolarized spectrum of Figure 2 was obtained from a random section of the blue crystal.

All spectra were measured at room temperature with a Cary-14 recording spectrophotometer. The standard sample compartment was replaced by a special housing which permitted the mounting of a Unitron MPS petrographic microscope in each of the sample and reference beams (in either the infrared or visible mode) in a manner similar to that of Burns (1966). The mineral specimen, mounted on the stage of the sample-beam microscope, was oriented in the polarized light beam so as to measure the desired spectrum, *i.e.*, parallel to a given crystallographic direction. Glan prisms were used as polarizers. Because the polarizers cannot be used above ∼ 25,000-$cm^{-1}$ unpolarized spectra were measured in the ultraviolet region (*e.g.* spectra marked UN in Figure 1a and 1c).

The trichroic scheme of the untreated tan zoisite can be appreciated through a study of the spectra of Figure 1. When the electric vector $E$, of the polarized light is parallel to $Z = a$, (*i. e.*, $E // Z = a$) the mineral section has a yellow-green colour due to the absorption of violet to blue light by the rather intense band centered at 22,500-$cm^{-1}$. Although the 16,800-$cm^{-1}$ band does absorb some yellow light, its intensity is weak relative to that at 22,500-$cm^{-1}$, and therefore the net result is the transmission of yellow-green light. Because the spectral features with maxima at 27,000-$cm^{-1}$ and 13,400-$cm^{-1}$ are both outside the visible region, *i.e.*, ∼ 25,000-$cm^{-1}$ (400nm) to ∼ 14,000-$cm^{-1}$ (700 nm), they do not influence the colour.

In the $E // Y = c$ spectrum, the two-component envelope (16,700 - 19,000 $cm^{-1}$) absorbs yellow-green light and the section thereby transmits blue light. The trough or valley centered at ∼ 22,000-$cm^{-1}$ (∼450 nm) can be thought of as a "window" for the blue light.

Similarly, in the $E // X = b$ spectrum, blue-green to yellow-green light is absorbed in the 17,000 to 19,000 $cm^{-1}$ region, and, the mineral section derives its red-violet colour from the combined transmission of violet light through the shallow "window" on the high-energy side of the absorption envelope, and of red light on its low-energy side.

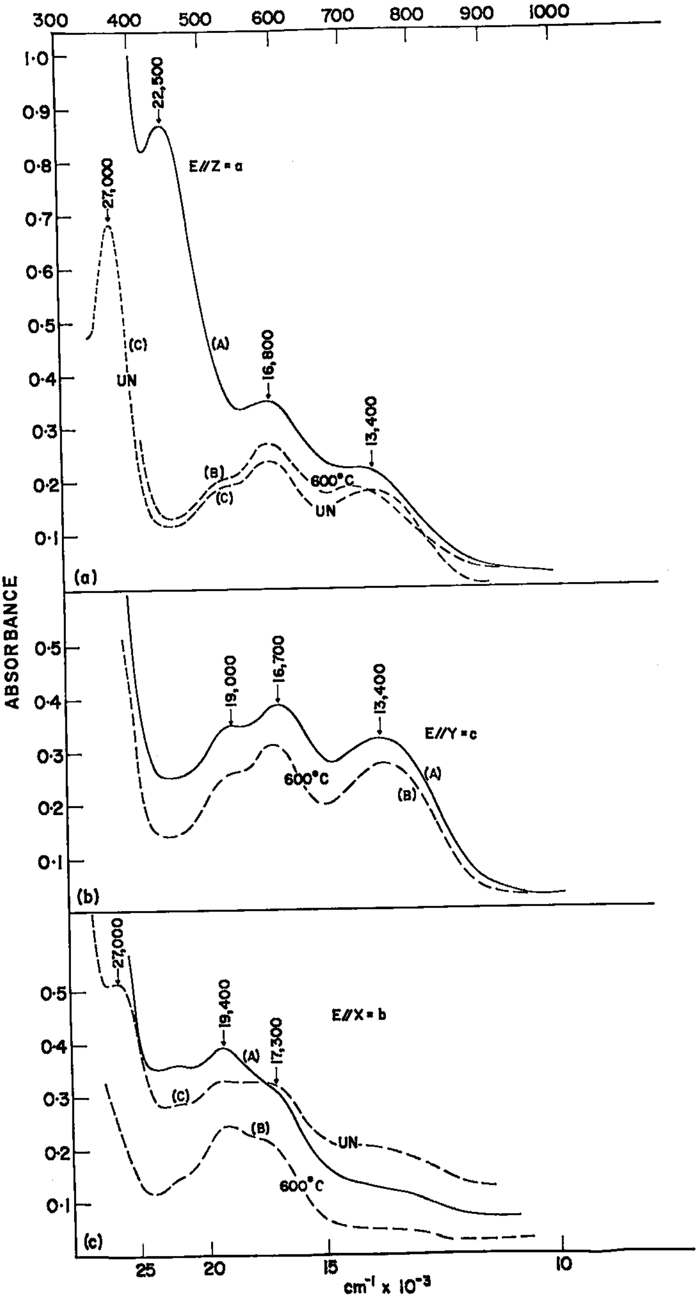
300
400
500
600
700
800
900
1000
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
ABSORBANCE
22,500
27,000
E//Z = a
(A)
(C)
UN
16,800
13,400
(B)
600°C
(C)
UN
(a)
19,000
16,700
13,400
E//Y = c
(A)
600°C
(B)
(b)
27,000
19,400
17,300
E//X = b
(A)
(C)
(B)
UN
600°C
(c)
25
20
15
10
$\text{cm}^{-1} \times 10^{-3}$

Fig. 1a. Spectra of an $a$-$c$ section of tan zoisite, thickness = 0.32 cm.
A $E // Z = a$ spectrum of untreated zoisite.
B $E // Z = a$ spectrum of zoisite after heating to 600°C.
C Unpolarized spectrum of zoisite after heating to 600°C.
Fig. 1b. Spectra of an $a$-$c$ section of tan zoisite.
A $E // Y = a$ spectrum of untreated zoisite.
B $E // Y = a$ spectrum of untreated zoisite after heating to 600°C.
Fig. 1c. Spectra of an $a$-$b$ section of tan zoisite, thickness = 0.18 cm.
A $E // X = b$ spectrum of untreated tan zoisite.
B $E // X = b$ spectrum of untreated tan zoisite after heating to 600°C.
← C Unpolarized spectrum of tan zoisite after being heated to 600°C.

As reported previously (Liddicoat & Crowningshield 1968; Hurlbut 1969), the trichroic tan zoisite becomes blue on heating; the spectral changes induced by such treatment are shown in Figure 1. Experiments indicated that there is no appreciable change on heating below 250°C. However, on heating the vanadium-zoisite, in either air or hydrogen, in the range ~450 to 650°C, spectral changes such as those indicated in Figure 1 are produced. It is evident that the colour change is primarily

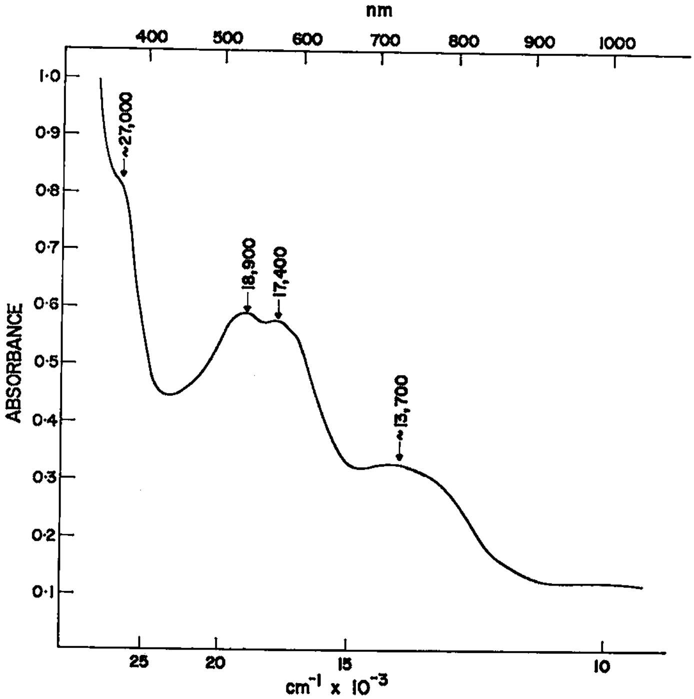

Fig. 2. Unpolarized spectrum of a random section of untreated blue zoisite, thickness = 0.26 cm.

the result of the disappearance of the 22,500-cm$^{-1}$ band from the $E$ // $Z$ = $a$ spectrum of the originally tan-coloured mineral. Figure 1 also shows that the $E$ // $Z$ = $a$ spectrum of the heat-treated zoisite is essentially the same as $E$ // $Y$ = $c$ spectrum of the untreated material, and this accounts for the change in the pleochroic scheme from trichroic to dichroic.

On the basis of the foregoing, then, the blue colour of the untreated zoisite, whose unpolarized spectrum is shown in Figure 2, can be attributed to the absence of the 22,500-cm$^{-1}$ band. These observations also suggest the possibility that the natural blue variety of zoisite may have been subjected to thermal conditions not experienced by the tan material.

Having described the polarized absorption-spectra of the vanadium-zoisite it is desirable now to attempt to explain the origin of the spectral features.

Analysis indicates that vanadium and titanium (in the trichoic variety) are the principal transition-metal ion impurities in zoisite, and it is reasonable to assume that the spectra are due to one, or both, of these ions substituting for aluminium on one, or both, of the two kinds of octahedral sites (Figure 3). However, the spectra should be dominated by features due to vanadium ions because of its much higher concentration in the mineral.

Because $V^5$ is a $d^0$ ion, it cannot give rise to intra-cationic electronic transitions; therefore, the spectra must be due to one or more of the chromogenic ions $V^{2+}$, $V^{3+}$ and $V^{4+}$.

Although $V^{2+}$ ($d^3$) theoretically has a complex absorption spectrum in the visible region, it is seldom observed and it is unlikely that this ion is present in zoisite because of its relatively large size (0.88Å) and low stability in an oxygen environment (Cotton & Wilkinson 1966, p. 817; Sturge, 1963).

As we will see, the presence of $V^{4+}$ in the Tanzanian zoisite cannot be completely discounted; however, it is probable that most of the spectral features of the spectra can be attributed to $V^{3+}$, an ion whose charge alone makes it a likely substitute for $Al^{3+}$. However, it will be evident that the trichroism of the tan variety of the mineral cannot be explained on the basis of this ion alone.

It is well known that the absorption spectrum of $V^{3+}$ ($d^2$) has three principal bands due to the spin-allowed transitions $^3T_1(F) \rightarrow {}^3T_2(F)$, $^3T_1 \rightarrow {}^3T_1(P)$ and $^3T_1 \rightarrow {}^3A_2(F)$ (for example see Cotton & Wilkinson 1966, p. 677). It is convenient to designate the spectral bands associated with these transitions as $\nu_1$, $\nu_2$ and $\nu_3$ respectively, in order of increasing energy. In the spectrum of $V^{3+}$-bearing corundum, for example, $\nu_1$, $\nu_2$

and $\nu_3$ are found at 17,500, 25,000 and 31,000 to 34,000 cm$^{-1}$ respectively (McClure 1962; McFarlane 1964).

Although the intensity of the background absorption, due to charge-transfer processes, increases rapidly in the ultraviolet region, it was possible to resolve the unpolarized spectrum of a thin *a*(Z)–*c*(*Y*) section of the tan zoisite to ~39,000 cm$^{-1}$. Because a significant shoulder was not found between 27,000 and 39,000 cm$^{-1}$, it is considered that the entire *d–d* spectrum of Tanzanian zoisite is in the range ~13,000 to 27,000 cm$^{-1}$, and that all the features present in the spectra are shown in Figure 1.

Because the 22,500-cm$^{-1}$ band is the only one affected by heating the tan zoisite (in air or hydrogen), it is unlikely that the band is part of the *d–d* spectrum of $V^{3+}$. As we have seen, the spectrum of $V^{3+}$ is complex and it would be expected that more than one band would disappear or change in intensity during the heat treatment. Thus, it seems necessary to assign the 22,500-cm$^{-1}$ band to either $V^{4+}$ or $Ti^{3+}$. Both of these ions have a $d^1$ configuration, and in octahedral coordination can give rise to the $^2T_2 \rightarrow {}^2E(D)$ transition. This point will be taken up in more detail below.

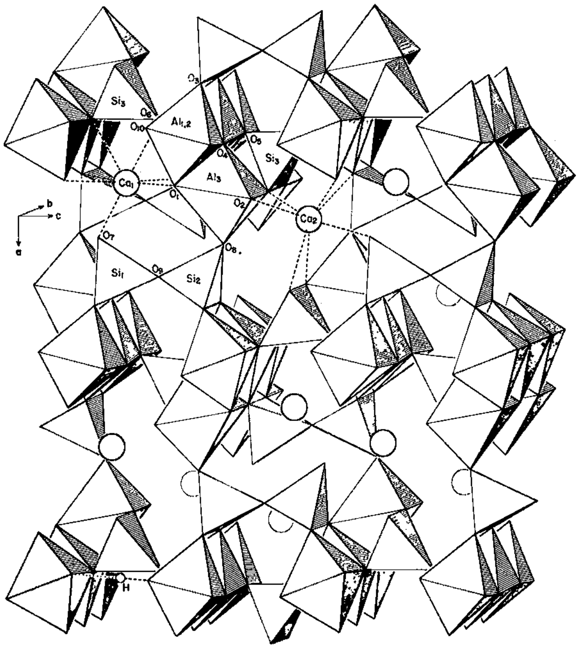

Fig. 3. The structure of zoisite as viewed nearly along the *b* axis, (after Dollase 1968).

On the basis of the foregoing, it can be concluded that the spectra of the heated tan zoisite and the natural blue material (Figure 2) are due to $V^{3+}$ alone, and that the broad, multi-component envelopes centered at ~13,500 and ~18,000-$cm^{-1}$ can be assigned to the $\nu_1$ and $\nu_2$ transitions respectively, while the 27,000 $cm^{-1}$ band is the result of the $\nu_3$ transition. Because of its size (0.74Å) and the fact that a $d^2$ ion gains considerable crystal-field stabilization energy on entering a distorted octahedral site (Schwarz 1967), it is probable that most of the $V^{3+}$ is located in the larger and more distorted $Al_3$ site of zoisite (Figure 3). The relatively low symmetry ($C_{2v}$) of the $Al_3$ site may also account for the splittings of the $\nu_1$ and $\nu_2$ absorption envelopes in the spectra of Figures 1 and 2. Attempts to work out selection rules based on $C_{2v}$ symmetry (using correctly chosen axes) were unsuccessful in explaining the polarization properties of all the spectral bands. However, it is worth noting that the polarization of the $\nu_3$ band (Figure 3a), which is present only in the $E // Z = a$ spectrum, can be accounted for on this basis with the ground state of $V^{3+}$ in the $Al_3$ site being $^3A_2$.

Figure 4 is a simplified energy-level diagram for a $d^2$ ion in an octahedral field (after Berkes 1968) when the Racah parameter, $B$, is 630 $cm^{-1}$. It is apparent that a good fit is obtained for the spectral features of $V^{3+}$-bearing corundum when the crystal-field parameter, $Dq$ is ~1,800 $cm^{-1}$. To achieve a fit for the $\nu_1$ and $\nu_3$ bands of the zoisite spectra, $Dq$ must be reduced to ~1,400 $cm^{-1}$; however, this places $\nu_2$ at ~20,000 $cm^{-1}$, a value that is high by 2,000 $cm^{-1}$. If the Racah parameter $B$, which is a measure of the separation of the free-ion terms $^3F$ and $^3P$, is less for the zoisite spectrum that for the corundum spectrum, then $\nu_2$ for the former could be placed closer to the observed value of ~18,000 $cm^{-1}$.

That the crystal field experienced by $V^{3+}$ in the Tanzanian zoisite is appreciably lower than in corundum may well reflect, in part, the difference in the sizes of the sites in the two minerals : the average Al–O bond distances for corundum and zoisite ($Al_3$) are 1.92Å and 1.97Å respectively. Nevertheless, the strength of the crystal field is rather low; in this connection it is noteworthy that the average Pauling bond strength for the $Al_3$ oxygens is 1.96 and that of the $Al_{1,2}$ oxygens is 2.06 (Dollase 1968).

It was suggested above that the highly polarized band at 22,500 $cm^{-1}$ was due to either $V^{4+}$ or $Ti^{3+}$. However, $Ti^{3+}$ is to be favoured because of its charge, and because the presence of the 22,500-$cm^{-1}$ band in the spectra of the trichroic variety of the Tanzanian zoisite seems to correlate directly with the presence of a significant concentration of titanium in the mineral.

Basing the calculations on total titanium concentration, the extinction coefficient for the 22,500-cm$^{-1}$ band is in the range 50 to 100 litre/mole-cm, which is appreciably higher than for the $V^{3+}$ spectral bands which are generally in the range 2 to 15 litre/mole-cm.

If the 22,500-cm$^{-1}$ band is due to the $^2T_2 \rightarrow {}^2E_2(D)$ transition of $Ti^{3+}$, its energy is appreciably higher than for $Al_2O_3$:$Ti^{3+}$. In corundum, the transition is found at ~19,000 cm$^{-1}$ (McClure 1962). Tentatively, the higher energy can be accounted for by assuming that $Ti^{3+}$ is ordered on the smaller $Al_{1,2}$ sites of zoisite, although it is not evident why this should be so.

A broad, highly polarized band at ~21,000 cm$^{-1}$, which is responsible for the pleochroism of andalusite, has recently been ascribed to $Ti^{3+}$ →

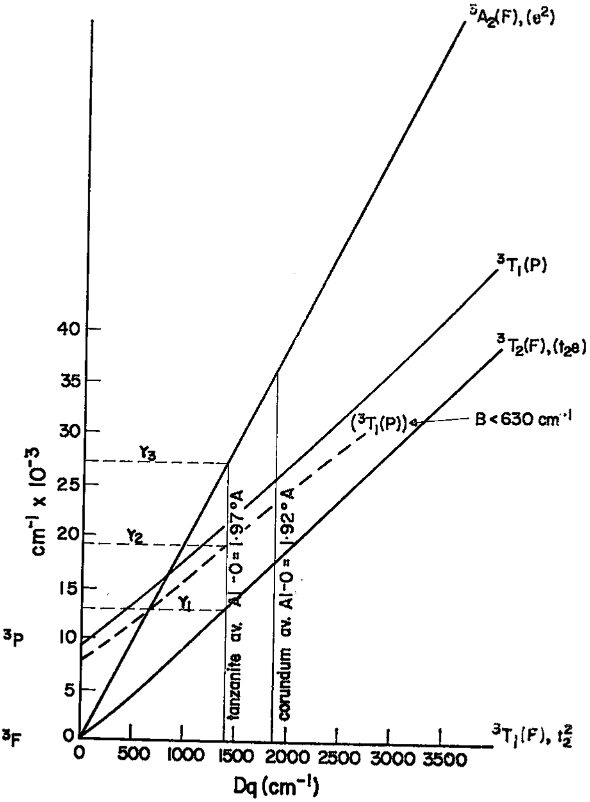

FIG. 4. Energy level diagram for $d^2$ electronic configuration in an octahedral field; $B = 630$ cm$^{-1}$ (after Berkes 1968).

$Ti^{4+}$ charge transfer (Faye and Harris 1969). However, this process cannot be invoked for the case of the Tanzanian zoisite because the polarization properties of the 22,500-$cm^{-1}$ band cannot be related to the $Al_{1,2}$–$Al_{1,2}$ or the $Al_{1,2}$–$Al_3$ vectors, *i.e.* the directions in which there is the possibility of overlap of $t_{2g}$ orbitals of titanium ions on adjacent octahedral sites.

Whether the 22,500-$cm^{-1}$ band is attributed to either $Ti^{3+}$ or $V^{4+}$, its polarization properties can be accounted for by using group theoretical arguments based on its site having $C_{2v}$ symmetry. In such calculations the symmetry axes (see Figure 3) are taken to be essentially coincident with the crystallographic axes, and the unique twofold axis is coincident with c.

In the $C_{2v}$ point group, the $T_{2g}$ and $E_g$ of the $^2T_{2g} \rightarrow {}^2E_g$ transition in $O_h$, transform as $A_1 + A_2 + B_2$ and $A_2 + B_2$, respectively (Wilson, Decius & Cross 1955). If $A_1$ is taken as the ground state for $Ti^{3+}$ (or $V^{4+}$) then it is found that a transition ($A_2 \rightarrow B_2$) is allowed only when $E$ // Z = *a*, a calculation that is in accord with observation (Figure 1a). The possibility that this agreement is coincidental cannot be discounted, however.

That the 22,500-$cm^{-1}$ band disappears on heating suggests a process in which $Ti^{3+}$ (or $V^{4+}$) is oxidized to $Ti^{4+}$ (or $V^{5+}$) *i.e.*, to a state with a $d^0$ configuration, which does not give rise to a *d–d* absorption spectrum. However, because the spectral band disappears on heating in hydrogen as well as in air, it is difficult to rationalize a mechanism that accounts for this proposal.

## ACKNOWLEDGMENTS

The authors are grateful to Dr. D. C. Harris for microprobe analyses, and to Mr. P. O'Donovan for assistance in preparing mineral sections. Special thanks are due to Dr. M. G. Townsend for helpful discussions.

## REFERENCES

ANDERSON, B.W. (1968) : Triple bill: Three items of interest to gemmologists. *J. Gemmol.* **11,** 1-3.

BERKES, J.S. (1968) : Energy level diagrams for transition metal ions in cubic crystal fields. *Monograph* **2,** *Materials Research Laboratory, The Pennsylvania State Univ., University Park, Penn.*

BURNS, R.G. (1966) : Apparatus for measuring polarized absorption spectra of small crystals. *J. Sci. Instrum,* **43,** 58-60.

COTTON, F.A. & WILKINSON, G. (1966) : *Advanced inorganic chemistry,* Second Ed. Interscience Publishers, Inc., New York.

DOLLASE, W.A. (1968) : Refinement and comparison of the structures of zoisite and clinozoisite. *Amer. Mineral.* **53,** 1882-1898.

Faye, G.H. & Harris, D.C. (1969) : On the origin of colour and pleochroism in andalusite from Brazil. *Can. Mineral.* **10,** 47-56.

Hurlbut, C.S. (1969) : Gem zoisite from Tanzania. *Amer. Mineral,* **54,** 702-709.

Liddicoat, R.T. & Crowningshield, G.R. (1968) : More about zoisite. *Lapidary J.,* **22,** 736-740.

McClure, D.S. (1962) : Optical spectra of transition-metal ions in corundum. *J. Chem. Phys.,* **36,** 2757-2779.

MacFarlane, R.M. (1964) : Optical and magnetic properties of trivalent vanadium complexes. *J. Chem. Phys.,* **40,** 373-377.

Meen, V.B. (1968) : Zoisite — a newly found gem from Tanzania. *Lapidary J.,* **22,** 636-637.

Schwarz, H.P. (1967) : The effect of crystal field stabilization on the distribution of transition metals between metamorphic minerals, *Geochim. Cosmochim. Acta,* **31,** 503-517.

Sturge, M.D. (1963) : Optical spectrum of divalent vanadium. *Phys. Rev.* **130,** 639-646.

Wilson, E.B., Decius, J.C. & Cross, P.C. (1955) : *Molecular vibrations.* McGraw-Hill, New York.

*Manuscript received April 1970, emended May 1970.*