Optical spectroscopic study of tuhualite and a re-examination of the beryl, cordierite and osumilite spectra

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ABSTRACT

Polarized optical absorption spectra of a rare Fe²⁺, Fe³⁺-bearing silicate mineral, tuhualite, (Na,K)₂Fe²⁺Fe³⁺Si₁₂O₃₀⋅H₂O, were measured at room temperature in the range 350–4000 nm (ca. 28500–2500 cm⁻¹). The spectra display a number of strongly pleochroic absorption bands in the visible and NIR range, which are attributed to ferric and ferrous ions distributed over octahedral and tetrahedral sites in the structure. No absorption bands caused by H₂O or OH stretching vibrations have been observed in the 3000 to 4000 cm⁻¹ range. A narrow, weak absorption line at ~422 nm (γ = β) is attributed to the ⁴A₁g → ⁴A₁g,⁴E_g spin-forbidden transition of six-coordinated Fe³⁺ ions that occupy the octahedral Fe2 position of the tuhualite structure.

A broad, intense band at ~573 nm (γ ≫ β ≫ α) is assigned to a Fe²⁺/Fe³⁺ intervalence charge transfer transition (IVCT) between tetrahedral Fe²⁺ and octahedral Fe³⁺. Together with the high-energy absorption edge, the band at 573 nm causes the intense violet color and spectacular pleochroism (γ > β > α) of tuhualite. An intense band at ~1040 nm (γ > β > α) and a much weaker band ~ 2150 nm (α) are attributed to spin-allowed dd transitions of Fe²⁺ in the strongly distorted tetrahedral Fe1 sites.

On the basis of the data obtained for tuhualite, optical spectra of the structurally related minerals beryl, cordierite, and osumilite are discussed and re-assigned. The spectra are re-interpreted on the basis of the distribution of Fe²⁺ in these minerals over structural octahedral and tetrahedral positions.

INTRODUCTION

The site occupancy of Fe²⁺ in ring silicates such as beryl and cordierite is controversial. In addition to occupation of an octahedral site, arguments have been presented in favor of additional Fe²⁺ being located in both an interstitial channel site and in a tetrahedral site. Tuhualite, a rare IV Fe²⁺-, VI Fe³⁺-bearing chain silicate found only in the comendites of Mayor Island, New Zealand, provides an opportunity to experimentally address this controversy. Hutton (1956) described the occurrence, physical properties, morphology and chemical composition of tuhualite. Merlino (1969) refined the crystal structure and proposed the formula, (Na,K)₂Fe²⁺Fe³⁺Si₁₂O₃₀⋅H₂O.

According to Merlino (1969), the structure of tuhualite (Fig. 1) consists of six-repeated double chains of silicon tetrahedra and chains of edge-sharing alternating Fe²⁺ tetrahedra and Fe³⁺ octahedra, labeled Fe1 and Fe2, respectively. Sodium atoms are found in an irregular sixfold coordination in open structural channels aligned parallel to the a axis. Water molecules were also assumed to occupy the channel sites. Merlino proposed that the structure of tuhualite was closely related to that of osumilite, formulated as (Na,K)₅(Mg,Fe²⁺)(Al,Fe³⁺)₅Si₁₀O₃₄·H₂O at that time.

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FIGURE 1. The view of a fragment of the tuhualite structure viewed down the a axis, based on the structural data of Merlino (1969). A zigzag-like chain of Fe²⁺ octahedra and distorted, edge-shared Fe³⁺ tetrahedra is parallel to the c axis. Six-coordinated Na⁺ ions are located in the structural channels.
Due to the structure and unusual (from the point of view of crystal field stabilization energy concepts) distribution of Fe$^{3+}$ and Fe$^{2+}$ ions among octahedral and tetrahedral sites, tuhualite seems to be an important phase for optical spectroscopic investigation. Particularly, it is likely to be a point of comparison for the interpretation of optical absorption spectra of other ring silicates such as beryl, cordierite and osmiumite. Indeed, the structures of all four minerals, tuhualite (Fig. 1), beryl, cordierite, and osmiumite, are similar. They all contain large channels composed of AlO$_4$ and SiO$_4$ tetrahedra, that are elongated along a in tuhualite (Fig. 1) and osmiumite, and along c in cordierite and beryl. The channels are interconnected by slightly distorted octahedra and strongly distorted edge-shared tetrahedra. Some studies (Price et al. 1976; Vance and Price 1984; Taran et al. 1989; Geiger et al. 2000a) argue that the tetrahedra in the beryl and cordierite structures accommodate some Fe$^{2+}$, which causes a pair of optical absorption bands in the near infrared range originating from the electronic spin-allowed $^5E ightarrow ^5T_2$ transition of $^{43}Fe^{2+}$. Goldman et al. (1977, 1978) and Goldman and Rossman (1978a) recognized that the energies of the bands (9000 to 10000 cm$^{-1}$) were greater than those reported for tetrahedral Fe$^{2+}$ at that time and bore more resemblance to those of large, strongly distorted octahedral sites and large sites of higher coordination number. For this reason they proposed that the bands in NIR spectra of beryl, cordierite and osmiumite are caused by spin-allowed $dd$ transitions of a small fraction of the total Fe$^{2+}$ that occupies irregular positions in the structural channels. Mineeva and Bershov (1990) have also suggested that in beryl most of the iron ions enter the structural channels as neutral or weakly charged positive complexes such as Fe$^{2+}$-O$_2^-$-Fe$^{2+}$-O$_2^-$, or Fe$^{2+}$-O$_2^-$-Fe$^{3+}$-O$_2^-$.

In this paper results of an optical spectroscopic study of deep-violet tuhualite from Mayor Island, New Zealand, are presented. The results obtained from tuhualite are then used to re-interpret the relevant spectroscopic features in the optical spectra of beryl, cordierite and osmiumite. Illustrative examples of synthetic hydrothermal iron-doped beryls are presented and discussed in more detail.

**EXPERIMENTAL DETAILS**

**Sample preparation**

Two microcrystals of tuhualite (Stanford mineral collection 52544) were used for optical spectroscopic investigation. Samples were prepared as thin sections using a glass plate for support and epoxy resin as the embedding material. The crystals were oriented in accordance with their morphological habit with well-developed c{001} and h{010} forms (Hutton 1956). Then they were polished on one side to thicknesses of ca. 24 µm and 16 µm, respectively. As a result one crystal was prepared as an $ab$ section ($\sim30 \times 50$ µm) appropriate for measuring $\alpha$ and $\beta$ polarized spectra. The other sample was the $ac$ section ($\sim20 \times 20$ µm) which allowed measurement of the $\alpha$ and $\gamma$ polarizations. Based on observation of conoscopic figures, orientation in the $ab$ section was accurate to within 5–8° and in the $ac$ section to within 2°.

Four samples of synthetic iron-doped beryl grown by the hydrothermal method (Lebedev et al. 1988) were studied to compare to tuhualite. The crystals were supplied by Alexander Lebedev (Novosibirsk, Russia) and were prepared as transparent, oriented, self-supporting platelets, polished on both sides. Chemical analyses of three of the crystals were obtained with a JEOL 733 electron microprobe using Na-, K-, and Ca-feldspars, TiO$_2$, and synthetic end-member Mg-, Fe-, and Co-olivines as standards. Results of the microprobe analysis, color and thickness are given in Table 1.

**Optical and IR spectroscopy**

Polarized optical absorption spectra in the 350–1700 nm range were obtained at about 1 nm resolution with a home-built microspectrometer system consisting of a 1024 element Si and a 256 element InGaAs diode-array detector coupled to a grating spectrometer system via fiber optics to a highly modified NicPlan infrared microscope containing a calcite polarizer. Pairs of conventional 40× and 10× objectives were used as an objective and a condenser. The optical spectrum of beryl A-673 was measured at temperatures from 295 to 80 K in the spectral range 350–1600 nm using a Linkam TMS 93 microscope cooling stage attached to the microspectrometer. To maintain thermal contact, the sample was attached to the sample holder with vacuum grease. The chamber was evacuated to $1 \times 10^{-2}$ – $5 \times 10^{-4}$ torr. To avoid moisture condensation, the external surfaces of the windows were continuously blown with dry air. The temperature stability was ±2 K within the entire temperature range studied.

In the spectral range 10000–2500 cm$^{-1}$, polarized spectra were measured with a Nicolet Magna-IR 860 FTIR spectrometer using an InSb detector, SiO$_2$ beamsplitter, quartz halogen lamp source and a LiIO$_3$ crystal polarizer. The spectral resolution was 4 cm$^{-1}$. The measurement area was defined by an aperture of 20 µm in diameter for tuhualite and 200 µm for beryl. Five hundred scans were collected for each spectrum.

Spectra in the different ranges were merged to a composite spectrum. In the case of the tuhualite spectra, sloping baselines in some ranges were first corrected before the spectra were merged. To evaluate energy, peak intensity and half-widths of the Fe$^{2+}$ spin-allowed bands, Peakfit 4.0 (Jandel Scientific) software was used to fit the spectra with Gaussian forms after they were first converted to a linear wavenumber scale. The number of components used in the fits was always chosen to be the number of bands estimated from visual inspection of the spectra. Raw spectral data are available at http://minerals.gps.caltech.edu/manuscripts/tuhualite/index.htm.

**TABLE 1.** Sample numbers, microprobe chemical composition, color and thickness of the samples of synthetic hydrothermal iron-doped beryls studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MnO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Σ</th>
<th>Color</th>
<th>Thickness, mm</th>
</tr>
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<tbody>
<tr>
<td>Fe-4-51</td>
<td>66.54</td>
<td>0.02</td>
<td>17.31</td>
<td>2.17</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>86.08</td>
<td>Colorless</td>
<td>2.203</td>
</tr>
<tr>
<td>A-671</td>
<td>65.29</td>
<td>0.00</td>
<td>16.06</td>
<td>4.05</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.42</td>
<td>0.02</td>
<td>85.86</td>
<td>Dark-blue</td>
<td>0.470</td>
</tr>
<tr>
<td>A-673</td>
<td>65.01</td>
<td>0.01</td>
<td>15.67</td>
<td>4.71</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.41</td>
<td>0.02</td>
<td>85.83</td>
<td>Dark-blue</td>
<td>0.431</td>
</tr>
</tbody>
</table>
RESULTS

Tuhualite

Polarized spectra of tuhualite in the 350–2670 nm range are shown in Figure 2. The spectra consist of a short-wave absorption edge and a series of bands, a to d, in the visible and NIR ranges, most of which have maximum intensity in β and γ-polarizations. A narrow, weak absorption line (a band, Fig. 2) at 422 nm is seen only in β and γ polarizations with an intensity ratio of 0:1:0.59:1. The ratio for band c at ~1040 nm is 0.06:1:0.53. Band d, at about 2150 nm, is weak and polarized in the α polarization (~1:0:0).

A first-order result is that there are no absorptions in the 4000–2500 cm⁻¹ range that might be interpreted as internal stretching vibrations of H₂O molecules in channel sites. This unambiguously shows that tuhualite is an anhydrous phase and that the chemical formula proposed by Merlino (1969) should not contain a water molecule.

Beryl

In the optical spectra of the synthetic beryls (Figs. 3–5) a series of absorption lines occur in the 950–1500 nm range. These are typical of natural (Wood and Nassau 1968) and synthetic hydrothermally grown beryls (Lebedev et al. 1988), and are caused by overtones and combination modes of channel H₂O molecules. In the spectrum of beryl Fe-4-51 (Fig. 3) lines of type-I H₂O (H-H direction || c) dominate, whereas in two other samples, A-671 (Fig. 4) and A-673 (Fig. 5), the lines from type-II H₂O (H-H direction ⊥ c) are prevalent. This is consistent with the much higher content of alkali ions, mostly Na⁺, in A-671 and A-673.

A relatively weak band system in the visible spectrum of beryl Fe-4-51 (Fig. 3) at ~870 nm, 625 nm, 428 nm and 371 nm, is undoubtedly caused by spin-forbidden electronic transitions in Fe³⁺ ions (d⁵ configuration), which substitute for Al³⁺ at the octahedral sites. Their assignment is shown in Figure 3.

Upon cooling from 295 K to 80 K, the band at ~830 nm

![Figure 3](image-url)
(E∥c) narrows slightly and increases in height (Fig. 5). Its integral intensity remains almost unchanged. The shape of the envelope in the E∥c-polarization, which includes the FeII/FeIII IVCT band and dd-bands of FeIII at 830 nm and 950 nm, changes with temperature. From visual observation it appears that the 950 nm band decreases in intensity and shifts to higher energy upon cooling. The IVCT band at ~690 nm appears to increase in intensity without any noticeable change in energy. A similar temperature behavior of these bands was observed in spectra of natural dark-blue beryls of a relatively high-iron content (Taran et al. 1989).

**DISCUSSION**

**Tuhualite**

From the chemical composition of tuhualite (Hutton 1956) one may expect that all the observed features (bands a to d) in the optical spectrum in Figure 2 are caused by Fe. The strict distribution of FeII and FeIII ions between, respectively, the octahedral Fe2 and the tetrahedral Fe1 sites of tuhualite (Merlino 1969) makes the interpretation of the bands straightforward.

The predominance of bands a, b, and c in the β and γ polarizations (Fig. 2) may be a result of an exchange-coupling interaction between FeII and FeIII. The exchange-coupling effect increases the intensity of dd transitions of certain transition metal ions such as Fe in adjacent sites compared to similar bands of “isolated” FeII and FeIII (Rossman 1988; Burns 1993). In tuhualite, such an interaction can only take place in the bc plane, where zigzagged chains of FeII-bearing tetrahedra and FeIII-bearing octahedra are elongated parallel to the c axis (Fig. 1).

**Spin-forbidden transitions of octahedral FeIII**

The weak and narrow a band in the tuhualite spectrum (Fig. 2) should be interpreted as a spin-forbidden $^4A_1g \rightarrow ^4A_1g, ^2E_g$ transition of six-coordinated FeIII in the Fe2 position. Because the other bands of FeIII are not as prominent, the $^4A_1g \rightarrow ^4A_1g, ^2E_g$ transition is frequently the only spectroscopic feature of FeIII easily seen in the spectra of iron-bearing minerals (e.g., Burns 1993). In the tuhualite spectrum, the comparatively low intensity of the a-band is due to its spin-forbidden character and the octahedral coordination of FeIII, wherein electronic transitions are usually less intense than those of tetrahedral coordination (Burns 1993). In wavelength (422 nm) and half-width, (~260 cm$^{-1}$) the a band of tuhualite is similar to a prominent, narrow band at ~427 nm in the spectra of natural iron-bearing beryls that is attributed to the $^4A_1g \rightarrow ^4A_1g, ^2E_g$ transition of FeIII in the octahedral (Al) positions of the beryl structure (Wood and Nassau 1968; Taran et al. 1989). The other bands originating from dd transitions of FeIII in tuhualite, $^4A_1g \rightarrow ^2T_1g$ and $^6A_1g \rightarrow ^2T_2g$, are not seen in the spectrum. Assuming that the electronic transitions of FeIII in tuhualite have approximately the same energies and relative intensities as in beryl (Fig. 3), it is obvious that the $^4A_1g \rightarrow ^2E_g$ (D) band is hidden by the intense UV absorption edge, and the $^4A_1g \rightarrow ^2T_1g$ and $^6A_1g \rightarrow ^2T_2g$ bands should be overlapped by the intense b and c bands.

Assuming that the FeO$_x$ content in tuhualite is 14.09 wt% (Hutton 1956), the ε value of a-band is calculated to be ~4 cm$^{-1}$-L-mol$^{-1}$, i.e., of the order of magnitude for spin-forbidden pair-enhanced dd transitions (Rossman 1996).

**FeII/FeIII intervalence charge transfer band**

The strong, broad b band (573 nm, ν$_{1/2}$ = 8,060 cm$^{-1}$) (Fig. 2) appears at approximately the same wavelength as the FeII/FeIII IVCT band in cordierite spectra (576 nm, ν$_{1/2}$ = 7,500 cm$^{-1}$), where it was assigned to the IVCT transition between FeII in the octahedron and FeIII in the T1 tetrahedron of the cordierite structure (Geiger et al. 2000b). Together with the high-energy absorption edge, the 573 nm band causes intense violet color and spectacular pleochroism (γ > β > α) of tuhualite.

Taking into account the distribution of FeII and FeIII in the tuhualite structure, one may confidently assume that the b-band is caused by IVCT between tetrahedral FeII and octahedral FeIII. To our knowledge, this is the only established example of an IVCT band of this type.

Polarization properties of the b band are consistent with its interpretation as FeII/FeIII IVCT. Indeed, numerous investigations have shown that IVCT bands in various minerals and compounds have maximum intensity when the E vector of the exciting light is oriented parallel to the FeII-FeIII bond (Robbins and Strens 1968). As seen in Figure 1, the zigzag chains of FeII tetrahedra and FeIII octahedra are parallel to the c axis in the bc plane of the tuhualite structure. Fe-Fe bonds make projections on the c and b axes, but not on the a axis. Therefore, the γ ≫ β ≫ α polarization of the b band is in agreement with this orientation. The direction cosines of the FeII-FeIII bonds calculated from the structural data of Merlino (1969), are 0.01, 0.55, and 0.84. From this, the theoretical ratio of the IVCT band is ~0:0.43:1. That is in reasonable agreement with the observed ratio ~0.07:0.59:1. The difference between theoretical and experimental values may arise, at least partly, due to convergence of the light beam in the condenser-objective system of the microscope-spectrophotometer used, which partly mixes polarizations (Goldman and Rossman 1978b), and minor misorientation of the samples studied.

Although in tuhualite the FeII/FeIII distribution is opposite
to that shown in cordierite (Geiger et al. 2000a, 2000b), the wavelength and half-width parameters of Fe\textsuperscript{2+}/Fe\textsuperscript{3+} IVCT bands are surprisingly close in both minerals. Unresolved shoulders at ~670 nm and ~503 nm on the low and high-energy wings of the \( b \) band in the tuhualite spectrum (Fig. 2) may be caused by spin-forbidden bands of \( ^{19}\text{Fe}^{2+} \), superimposed on the \( ^{19}\text{Fe}^{2+}/^{19}\text{Fe}^{3+} \) IVCT band. Due to the non-centrosymmetric character of the Fe\textsuperscript{2+} site and the high concentration of Fe in tuhualite, the spin-forbidden bands may be strong enough to be seen in the spectra. In cordierite spectra, a few spin-forbidden bands of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} are also superimposed on the \( ^{19}\text{Fe}^{2+}/^{19}\text{Fe}^{3+} \) IVCT band (Faye et al. 1968), another similarity between the spectra of the two minerals.

Tetrahedral ferrous iron

Bands \( c \) and \( d \) remain the only spectroscopic features in Figure 2 that may be attributed to spin-allowed \( dd \) transitions of Fe\textsuperscript{2+} in the tetrahedral sites of tuhualite. Although the energy of the \( c \) band is more typical of a spin-allowed transition of octahedral Fe\textsuperscript{2+} (e.g., Burns 1993), we propose that the \( c \) and \( d \) bands are caused by spin-allowed transitions (derived from the \( ^{3}E \rightarrow ^{3}T_{2} \) transition in \( T_{d} \) symmetry) of Fe\textsuperscript{2+} in the strongly distorted tetrahedral Fe1-site of the tuhualite structure. The splitting of the bands would result from distortion of the site. According to Merlino (1969), the point symmetry of the site is \( C_{2v} \), where the twofold axis is parallel to the crystallographic \( a \) axis (Fig. 2). Formally, all \( dd \) transitions originating from the split components of the \( ^{3}E \) and \( ^{3}T_{2} \) levels are allowed by the selection rules (Marfunin 1979). The pronounced difference in intensity of the \( c \) and \( d \) bands, however, is not explained by this theoretical model. Nevertheless, the crystal chemistry of tuhualite and criteria developed in the recent investigation of Rossman and Taran (2001) allow us to assert that the \( c \) and \( d \) bands are caused by spin-allowed \( dd \) transitions of \( ^{19}\text{Fe}^{2+} \).

Band intensity

The first criterion, the molar absorption coefficient (\( \varepsilon \)), of the \( c \) band (\( \beta \) and \( \gamma \) polarization) is consistent with the assignment of the \( c \) band to the distorted tetrahedral site. Under the assumption that the FeO content of tuhualite is 9.58 wt% (Hutton, 1956), \( \varepsilon \) for the \( \gamma \)-polarized component is calculated to be ~72 cm\(^{-1}\)L·mol\(^{-1}\). This value is typical for spin-allowed \( dd \) bands in \( ^{19}\text{Fe}^{2+} \)–bearing minerals (Rossman and Taran 2001). In the \( \beta \) polarization, where the \( c \) band has maximum intensity, the value of \( \varepsilon \) (135 cm\(^{-1}\)L·mol\(^{-1}\)) is practically the same as the value for osmilibite (130 cm\(^{-1}\)L·mol\(^{-1}\)) estimated by Goldman and Rossman (1978a) and close to the lower limit, 160 cm\(^{-1}\)L·mol\(^{-1}\), observed for beryl (Goldman et al. 1978). The \( \varepsilon \) value of the \( c \) band in the \( \beta \) polarization is subject to uncertainty because the thickness of the sample, ~24 \( \mu \)m, measured optically in a thin section that was polished on only one side, is inexact. Furthermore, it is likely that the composition of Hutton (1956) used for calculation is also inexact. It shows 1.99 wt% of H\(_{2}\)O content which is not consistent with our spectroscopic observations.

Band energy

The second criterion, the average energy of the \( c \) and \( d \) bands (7050 cm\(^{-1}\)), known as the barycenter, is consistent with the distortion of the Fe1 site in terms of bond-length (BLDP) and edge-length (ELDP) distortion parameters (Griffen and Ribbe 1979). As seen in Figure 6, tuhualite follows the correlation between these two parameters found by Rossman and Taran (2001) for a series of \( ^{19}\text{Fe}^{2+} \)-bearing oxygen-based minerals. This may be regarded as additional evidence that bands \( c \) and \( d \) in the tuhualite spectrum are caused by spin-allowed \( dd \) transitions of Fe\textsuperscript{2+} ions in the strongly distorted tetrahedral Fe1 sites.

The ratio of intensities, the splitting and the polarization of the bands \( c \) and \( d \) markedly resemble those of bands caused by spin-allowed \( dd \) transitions of Fe\textsuperscript{2+} ions in spectra of eudialyte, Na\(_{15}\)Ca\(_{6}\)Fe\(_{3}\)Zr\(_{3}\)Si\(_{26}\)O\(_{73}\)(O,OH), (Cl,OH)\(_{2}\), and, especially, gillespite, BaFe\(_{3}\)Si\(_{3}\)O\(_{10}\) (Pol’shin et al. 1991; Burns et al. 1966; Rossman and Taran 2001). Although a square-planar oxygen coordination of \( ^{19}\text{Fe}^{2+} \) in the latter minerals is usually regarded as a limiting case of a strongly tetragonally distorted octahedron (e.g., Burns at al. 1966), it may be also regarded as an extremely distorted tetrahedron. According to the (ELDP+BLDP) distortion parameter (0.1412), tuhualite holds an intermediate position between other \( ^{19}\text{Fe}^{2+} \)–bearing minerals with tetrahedral coordination of Fe\textsuperscript{2+} (gehlenite, pellylite, spinel, and staurolite) and eudialyte and gillespite, with square-planar coordination (Table 3 of Rossman and Taran 2001). This may explain why the spectroscopic characteristics of the \( c \) and \( d \) bands in tuhualite resemble both those of tetrahedrally coordinated Fe\textsuperscript{2+} (intensity of the \( c \) band, the relation between distortion and energy of the barycenter) and those of Fe\textsuperscript{2+} in square-planar configuration (ratio of band intensities).

COMPARISON TO OTHER RING SILICATES

The spectroscopic data on tuhualite provide insight into some of the features of the optical absorption spectra of beryl, cordierite, and osmilibite, minerals that are structurally related to tuhualite.

Spin-allowed \( dd \) bands of octahedral Fe\textsuperscript{2+}

When the spectrum of tuhualite (Fig. 2) is compared to those of beryl, cordierite and osmilibite (Goldman et al. 1977, 1978;
Goldman and Rossman 1978a; Platonov et al. 1979; Geiger et al. 2000a), two facts become obvious. The first is that the tuhualite spectrum does not contain bands that arise from spin-allowed transitions of Fe$^{2+}$ in octahedral coordination. Such bands in beryl, cordierite and osmiumite spectra appear in the 830–1430 nm range. They are relatively weakly split into two components, which is consistent with the modest distortions of the octahedral sites in the structures of these minerals. As an example, polarized spectra of synthetic hydrothermal, dark-blue, Fe-doped beryls A-671 and A-673 with high Fe contents are shown in Figures 4 and 5, respectively. The two bands in E||c polarization around 833 nm and 952 nm, labeled in Figure 4 as $^{\text{IV}}$Fe$^{2+}$, are the bands under consideration. Their intensity is much higher in A-673 than in A-671, although the difference in Fe content in the samples is not large (Table 1). Assignment of these bands to $^7T_2g \rightarrow ^3E_g$ transitions of Fe$^{2+}$ and absorption lines caused by overtones and combination modes of type II-channel water molecules (in Fig. 4 these features are marked as H$_2$O$_{\text{mann}}$) are correlated. Because type II-H$_2$O molecules are related to neighboring alkali ions in the structural channels (Wood and Nassau 1968), this correlation suggests that with an increase of $^{3}$Fe$^{2+}$ the content of channel Na$^+$ ions also increases due to the Al$^{3+}$→$^{3}$Fe$^{2+}$ + Na$_{\text{mann}}$ substitution. This further supports the assignment of both the 830 nm and 950 nm (E||c) bands in the spectra of iron-bearing beryls to $^{3}$Fe$^{2+}$.

In the optical spectra of both natural and synthetic iron-bearing beryls, the intensities of the $^7T_2g \rightarrow ^3E_g$ bands of $^{3}$Fe$^{2+}$ and absorption lines caused by overtones and combination modes of type II-channel water molecules (in Fig. 4 these features are marked as H$_2$O$_{\text{mann}}$) are correlated. Because type II-H$_2$O molecules are related to neighboring alkali ions in the structural channels (Wood and Nassau 1968), this correlation suggests that with an increase of $^{3}$Fe$^{2+}$ the content of channel Na$^+$ ions also increases due to the Al$^{3+}$→$^{3}$Fe$^{2+}$ + Na$_{\text{mann}}$ substitution. This further supports the assignment of both the 830 nm and 950 nm (E||c) bands in the spectra of iron-bearing beryls to $^{3}$Fe$^{2+}$.

In the spectra of cordierite and osmiumite, the bands assigned to spin-allowed $dd$ transitions of $^{3}$Fe$^{2+}$, appear at 995 nm and 1170 nm (a polarization) and 980 nm and 1425 nm (E||c), respectively.

The lack of octahedral Fe$^{2+}$ bands in the tuhualite spectrum (Fig. 2) supports the crystal-chemical formula of this mineral proposed by Merlino (1969), in which the octahedral sites are occupied by Fe$^{3+}$ ions. We use this fact to add support to the attribution of similar bands to $dd$ transitions of $^{3}$Fe$^{2+}$ ions in the spectra of beryl, cordierite and osmiumite. Indeed, in contrast to tuhualite, under our re-assignment, Fe$^{2+}$ in these minerals predominantly occupies octahedral sites as established by both optical absorption and Mössbauer spectroscopy (e.g., Price et al. 1976; Platonov et al. 1979; Goldman et al. 1977; Goldman and Rossman 1978a; Geiger et al. 2000a).

**Spin-allowed $dd$ bands of tetrahedral Fe$^{2+}$ in ring silicates**

The second conclusion, arising from the comparison of the optical spectra of tuhualite with published spectra of beryl, cordierite, and osmiumite, is that in the latter three minerals the correlated pair of absorption bands near 1000 nm and 2000 nm are analogous to the $c$ and $d$ bands in the tuhualite spectrum. It is these bands that have previously been attributed to both $^{3}$Fe$^{2+}$ (Price et al. 1976; Vance and Price 1984; Taran et al. 1989; Geiger et al. 2000a) and $^{3}$Fe$_{\text{channel}}$ (Goldman et al. 1977, 1978; Goldman and Rossman 1978a). As in tuhualite, where these bands must arise from $^{3}$Fe$^{2+}$ ions on Fe1 sites (see above), in the beryl, cordierite and osmiumite spectra they should be assigned to spin-allowed $dd$ transitions of Fe$^{2+}$ substituting for Be$^{2+}$ and Al$^{3+}$ions in strongly distorted tetrahedral sites that are structurally related to the Fe1 site in tuhualite. In the spectrum of synthetic beryl (Fig. 4) the pair of bands at 830 nm (E$\perp$e) and ~2060 nm (E||c) are labeled as $^{3}$Fe$^{2+}$. The intensity ratios of these bands in the synthetic Fe-doped beryl spectrum (Fig. 7) are in accordance with the ratios found by Goldman et al. (1978) for natural samples. This suggests that, in both cases, these bands are caused by iron and arise from the same site. In cordierite and osmiumite spectra, bands of this type appear at ~935 nm and 2230 nm (Goldman et al. 1977) and ~975 nm and ~2135 nm (Goldman and Rossman 1978a), respectively. It is characteristic that in tuhualite and beryl, cordierite and osmiumite, the intensity of the higher energy band is greater than the lower energy one. Also, in the four minerals these two bands appear in different polarizations. In the tuhualite spectrum (Fig. 2) the higher energy $c$ band is mostly polarized in $\beta$ and $\gamma$, whereas the lower energy $d$ band has strict $\alpha$ polarization. Also in beryl (Fig. 4), the higher energy band has E$\perp$e polarization while the low energy one is completely polarized in E||c. All this may be regarded as additional evidence that in the spectra of tuhualite, beryl, cordierite, and osmiumite the bands in question are of the same origin. It follows from the interpretation of the tuhualite spectrum discussed above that they are caused by spin-allowed $dd$ transitions of Fe$^{2+}$ ions in strongly distorted tetrahedral structural sites.

Previously Rossman and Taran (2001) observed a correlation between the barycenter energy and the distortion of four-coordinated sites (BLDP+ELDP) in a series of $^{3}$Fe$^{2+}$-bearing minerals. Beryl, cordierite and osmiumite plot in the general area of the correlation but are above the trend of the other minerals (Fig. 6). This may be explained by the fact that in beryl, cordierite and osmiumite the edge-shared tetrahedral sites are much smaller than in the other minerals. For the $^{3}$Fe$^{2+}$-bearing minerals studied by Rossman and Taran (2001) and tuhualite studied in this work, the average metal-ligand distances of tetrahedral sites are about 2 Å. Only for gehlenite is it shorter, 1.883 Å. In beryl, cordierite and osmiumite, <Be-O> and <Al-O> distances in the tetrahedral site are considerably

**Figure 7.** Correlation between the intensity of the ~830 nm (E$\perp$e) and ~2060 nm (E||c). Bands assigned to $^{3}$Fe$^{2+}$ in natural beryls (points from Goldman et al. 1978) and synthetic beryls (crosses).
smaller: 1.712, 1.755, and 1.767 Å, respectively. Therefore, in these minerals the crystal field strength of Fe$^{2+}$, which strongly depends on the mean metal-ligand distance in a coordination polyhedron (e.g., Burns 1993), should be noticeably larger. This in turn causes an increase of the band energies and shifts the barycenters to energies higher than the trend shown in Figure 6. As was stated by Geiger et al. (2000a), the relatively small volumes of the sites in question may be a cause of the relatively small fractions of $^{6i}$Fe$^{3+}$ in beryl, cordierite, and osmilibite.

The proportion of Fe in the tetrahedral site may be estimated from optical spectra and microprobe composition of samples assuming that ε values for the $^{3i}$Fe$^{2+}$ bands in these minerals are close to that in tuhualite, 135 cm$^{-1}$·L·mol$^{-1}$.

Judging from its spectra in Figure 4, the concentration of $^{3i}$Fe$^{2+}$ in the synthetic high-iron beryl A-671 is the highest of any beryl studied so far. Assuming a specific gravity of 2.70, any beryl studied so far. Assuming a specific gravity of 2.70, minerals are close to that in tuhualite, 135 cm$^{-1}$

Fe$^{3+}$ are accommodated in adjacent octahedral and tetrahedral structural sites. That is about 16% of the total Fe content. This value is commensurate with ~10% of $^{3i}$Fe$^{2+}$ per Fe$_{\text{tot}}$ in natural cordierite (Geiger et al. 2000a).

Because the ε values are almost the same for tuhualite and osmilibite, the proportion of $^{3i}$Fe$^{2+}$ in osmilibite from Nain, Labrador, 36% of the total Fe, is almost unchanged from Goldman and Rossman’s (1978a) estimate of about 40% of the total Fe. Goldman and Rossman (1978a) proposed that this Fe was in the channels but is now re-assigned to tetrahedral sites.

Fe$^{2+}$/Fe$^{3+}$ IVCT bands in ring silicates

Fe$^{2+}$/Fe$^{3+}$ IVCT bands appear in the spectra of tuhualite, beryl, cordierite and osmilibite. Under the re-interpretation that there is no Fe in their channels, the polarization of the IVCT bands in cordierite and osmilibite spectra indicate that Fe$^{2+}$ and Fe$^{3+}$ are accommodated in adjacent octahedral and tetrahedral structural sites. Although in tuhualite the distribution of ferrous and ferric ions among such sites is just the opposite of that in cordierite (Geiger et al. 2000a, 2000b), Fe$^{3+}$ in tetrahedral and Fe$^{2+}$ in octahedral sites, polarization properties of the IVCT band in the two minerals, tuhualite and cordierite, are similar.

In beryl the Fe$^{2+}$/Fe$^{3+}$ IVCT band that appears at ~690 nm in E∥c polarization indicates that the charge transfer takes place in the direction perpendicular to the octahedral-tetrahedral bonds in the structure. As this band appears only in samples, both natural and synthetic, having a relatively high intensity of spin-allowed $^{4}S^2$Fe$^{2+}$ bands, the octahedral Fe$^{2+}$ ions are undoubtedly involved in the IVCT process. Goldman et al. (1978) found that the intensity of the IVCT band correlates with the intensity of the spin-allowed $^{4}S^2$Fe$^{2+}$ dd bands. Because of this correlation, they assumed that IVCT takes place between $^{4}S^2$Fe$^{2+}$ and $^{4}S^2$Fe$^{3+}$ in, most likely, interstitial sites. Taking into account the E∥c polarization of the Fe$^{2+}$/Fe$^{3+}$ IVCT band in beryl, Platonov et al. (1979) proposed that it results from charge transfer between $^{4}S^2$Fe$^{3+}$ and $^{4}S^2$Fe$^{2+}$, where the superscript $6i$ refers to a six-coordinated interstitial position. $^{6i}$Fe$^{3+}$ is accommodated in the trigonal prism interstitial site between octahedral sites at z and z ± . Such an interpretation explains the main properties of the band: E∥c-polarization, energy typical of Fe$^{2+}$/Fe$^{3+}$ IVCT between edge-shared octahedral sites (Burns 1993), and the dependence of the intensity on the concentration of Fe$^{3+}$. It is also consistent with the temperature behavior of the band. Upon cooling to 80 K, the intensity of the 690 nm (E∥c) band increases (Fig. 6). Such behavior is typical of Fe$^{2+}$/Fe$^{3+}$ IVCT transitions (Smith and Strens 1976, Smith 1977, Taran and Langer 1998).

The entry of the Fe$^{3+}$ ion into the interstitial site between two octahedra that are very likely occupied by Fe$^{2+}$ ions provides local charge compensation through the substitution, 3Al$^{3+}$→3$^{4}S^2$Fe$^{2+}$ + $^{4}S^2$Fe$^{3+}$. In beryls of high iron content, charge compensation is accompanied with the substitution, Al$^{3+}$→$^{4}S^2$Fe$^{2+}$ + Na$^{+}$substitution. From the spectrum of Fe$^{3+}$-bearing beryl Fe$^{3+}$-4.51 (Fig. 3) and its composition (Table 1), the ε value of the $^{4}A_{1g}→{^4}A_{1g}E_{g}$ Fe$^{3+}$ band is found to be ~0.36 cm$^{-1}$·L·mol$^{-1}$. This is an order of magnitude less than for tuhualite (~4 cm$^{-1}$·L·mol$^{-1}$), where the absorption bands are assumed to be enhanced by pair interaction (see above). From the spectrum in Figure 4, one can determine that in beryl A-671 about 40% of the total Fe enters octahedral sites as Fe$^{3+}$. Fourteen percent of the total Fe occupies tetrahedral Be sites as Fe$^{2+}$. Therefore, about 46% of the total Fe enters octahedral Al sites as Fe$^{2+}$ and the interstitial sites as Fe$^{3+}$ ions. From the Na content of the sample (Table 1) it is possible to calculate that about 30% of total Fe enters the structure as Fe$^{3+}$ through the Al$^{3+}$→$^{4}S^2$Fe$^{2+}$ + Na$^{+}$substitution. The remainder (~16% of total iron) enters the beryl structure through the 3Al$^{3+}$→3 $^{4}S^2$Fe$^{3+}$ + $^{4}S^2$Fe$^{2+}$ substitution.

Models for the assignment of Fe to the structural channels (Mineeva and Bershov 1990) are not consistent with the intensity correlation of the Fe$^{2+}$/Fe$^{3+}$ IVCT band with the concentration of Fe$^{2+}$ in octahedral sites of the beryl structure.

ACKNOWLEDGMENTS

Gordon Brown (Stanford University) provided the tuhualite crystals from Hutton’s original collection. Alexander Lebedev (deceased) provided the synthetic beryls used in this study. Charles A. Geiger (Kiel, Germany) provided a helpful and thorough review that improved the quality of the paper. This project was funded in part by the National Science Foundation (U.S.A.) grant NSF EAR-9804871.

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MANUSCRIPT RECEIVED OCTOBER 26, 2000
MANUSCRIPT ACCEPTED APRIL 24, 2001
MANUSCRIPT HANDLED BY CELIA MERZBACHER