Visible-Region Absorption Spectra of a Ti³⁺ Fassaite from the Allende Meteorite: A Discussion

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Abstract

The spectral data of Dowty and Clark for the titaniferous pyroxene in the Allende meteorite have been reinterpreted. Arguments are presented in support of an alternative assignment of the two absorption bands at 21,000 cm⁻¹ and 16,500 cm⁻¹ as both being due to crystal field transitions in Ti^{3+} ions. Not only are two such bands expected for Ti^{3+} ions in distorted $M1$ coordination sites of clinopyroxenes, but the derived spectral parameters α and Δ_o are consistent with other Ti(III) compounds. The occurrence of Ti^{3+} ions in the clinopyroxene structure is attributed to the enhanced crystal field stabilization energy acquired in the $M1$ site.

Introduction

Dowty and Clark (1973) have described the crystal chemistry of an intriguing titaniferous pyroxene from the Allende meteorite, to which they ascribe the chemical formula:

$$Ca_{1.01}Mg_{0.38}Ti^{3+}_{0.34} \quad Ti^{4+}_{0.14} \quad Al_{0.87}Si_{1.26}O_6$$

Absorption bands in the optical spectra were observed at 21,000 cm⁻¹ and 16,500 cm⁻¹ in good agreement with results obtained for titaniferous pyroxenes from Apollo 11 rocks (Burns, Abu-Eid and Huggins, 1972). Burns *et al* (1972) assigned the two bands at 21,500 and 16,000 cm⁻¹ in the lunar pyroxenes to crystal field transitions in Ti^{3+}. However, Dowty and Clark (1973) assigned only one band (21,000 cm⁻¹) in their spectra to a Ti^{3+} crystal field transition. The other band (16,500 cm⁻¹) they attributed to a Ti^{3+}–Ti^{4+} charge-transfer transition.

We wish to prove that the spectral assignment proposed by Dowty and Clark (1973) is unlikely and to demonstrate that *both* bands are due to crystal field transitions in Ti^{3+}, the excited state of which is split into two energy levels in a distorted coordination site. We shall also indicate the significance of the results to the electronic structure and stability of Ti^{3+} ions in clinopyroxene structures.

Interpretation of the Spectra

To support our interpretation that titanium-related spectral features of the Allende and Apollo 11 pyroxenes in the visible region are due only to crystal field transitions in Ti^{3+} ions, we cite arguments based on (a) correlations with the spectra of Fe^{2+} ions in calcic clinopyroxenes; (b) analogies with the spectra of Ti(III) salts and complexes; (c) the nature of the $M1$ coordination site in calcic clinopyroxenes; (d) crystal field states of Fe^{2+} and Ti^{3+} ions in the $M1$ sites; (e) positions of absorption bands in relation to the spectro-chemical series; and (f) intensities of absorption bands for metal-metal charge transfer transition.

(a) Correlations with Fe^{2+} Spectra in Calcic Clinopyroxenes

Absorption spectra of clinopyroxene minerals are often complicated by contributions from Fe^{2+} ions in two coordination sites, $M1$ and $M2$, and by Fe^{2+}–Fe^{3+} charge transfer bands. The spectra of diopsides-hedenbergites containing negligible Fe^{3+} ions and with Ca^{2+} ions completely filling $M2$ positions show two absorption bands centered at 9,600 cm⁻¹ and 8,500 cm⁻¹. The most intense band occurs at 9,600 cm⁻¹ in the b = beta polarized spectrum and is distinctly polarization dependent. The spectra represent crystal field transitions in Fe^{2+} ions located in $M1$ positions of the clinopyroxene structure. In calcium deficient pyroxenes additional bands around 1000 nm (10,000 cm⁻¹) and 2200 nm (4,500 cm⁻¹) appear from Fe^{2+} ions in the $M2$ positions, while the presence of Fe^{3+} ions leads to a charge transfer band centered between 700 and 800 nm (approximately

12,000–14,000 cm^{-1}). The latter feature is demonstrated by the spectra (Fig. 1) of a hedenbergite, $Ca_{0.95}Mg_{0.20}Fe_{0.85}Si_2O_6$, containing about 5 percent ferric iron. The spectra show a prominent Fe^{2+}–Fe^{3+} charge transfer band around 12,200 cm^{-1}. The most significant features of the iron clinopyroxene spectra to the present discussion are: (1) the pronounced polarization dependence of the Fe^{2+} crystal field spectra; (2) the presence of the Fe^{2+}–Fe^{3+} charge transfer band *in all three* polarized spectra; and (3) the 1000–1500 cm^{-1} splitting in the crystal field spectra of Fe^{2+} ions in $M1$ positions. Similar split-
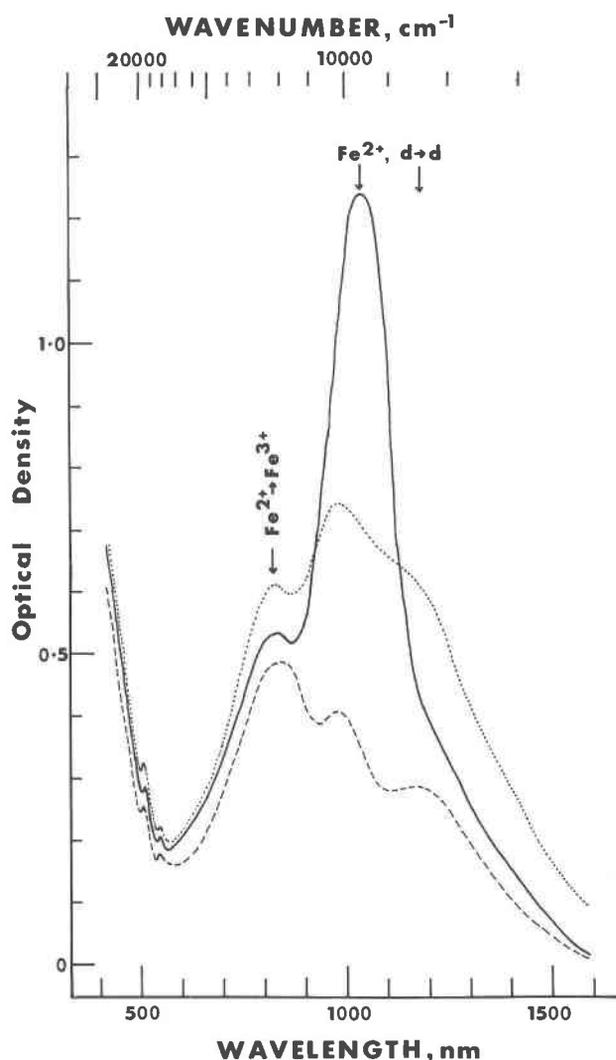

FIG. 1. Polarized absorption spectra of a hedenbergite. The calcic clinopyroxene has the formula $Ca_{0.95}Mg_{0.20}Fe_{0.85}Si_2O_6$ and contains 25.78 percent FeO and 1.53 percent Fe_2O_3. It is specimen 2B in Mueller (1960) *Amer. J. Sci.* **258**, 449. · · · · · α spectrum;———— β spectrum; ------ γ spectrum (Optic orientation: $\alpha{:}a = 34°$; $\beta = b$; $\gamma{:}c = 48°$).

tings are observed in the spectra of Ti(III) compounds.

(b) Analogies with the Spectra of Ti(III) Compounds

In a classical study of several hydrated Ti(III) compounds, Hartmann and Schläfer (1951) demonstrated that the spectra of octahedral $Ti(H_2O)_6{}^{3+}$ ions consist of an asymmetric absorption band with a prominent shoulder on the long wavelength side. The spectrum of cesium titanium alum, for example, was resolved into two peaks at 19,900 cm^{-1} and 18,000 cm^{-1} (Schläfer, 1964), indicating a splitting of about 1,900 cm^{-1} in the high energy crystal field states of Ti^{3+}. Similar energy separations of up to 4000 cm^{-1} have been observed in the absorption spectra of a variety of Ti(III) compounds (Hartmann *et al*, 1957; Hoff and Brubaker, 1971; Clark, 1968, p. 153). Clark (1968, p. 156) cites one exceptionally large splitting, involving the $[Ti(H_2O)_4F_2]^+$ ion, which appears to be as much as 8000 cm^{-1}. Other examples are given in Table 1. Similar energy separations have also been demonstrated in simple Fe(II) compounds (Cotton and Meyers, 1960). Thus, asymmetric or double-maxima absorption bands are prevalent in the crystal field spectra of octahedrally coordinated Fe^{2+} *and* Ti^{3+} ions.

(c) Nature of the Clinopyroxene M1 Coordination Site

Warren and Bragg (1928) originally demonstrated that the oxygen environment about the $M1$ position in diopside is appreciably distorted from octahedral symmetry (Figure 2). This has been confirmed and demonstrated in recent crystal structure refinements of a variety of clinopyroxenes (Prewitt and Burnham, 1966; Freed and Peacor, 1967; Peacor, 1967; Christensen and Hazell, 1967; Clark *et al*, 1969; Schropfer, 1971). In diopside, for example, metal-oxygen distances in the $M1$ site range from 2.115 Å to 2.050 Å (Table 2), while there is considerable variation of oxygen-oxygen distances and O–$M1$–O bond angles around the $M1$ "octahedron" (Clark *et al*, 1969). The structural data cited by Dowty and Clark (1973) for the titaniferous pyroxene in the Allende meteorite further demonstrate the asymmetry of the $M1$ coordination site. The range of metal-oxygen distances, 2.120 to 1.993 Å, is almost twice that observed in the diopside $M1$ site, suggesting increased distortion of the Allende pyroxene $M1$ site (containing Ti^{3+}) compared to

diopside. Such distortion profoundly affects the energy levels of Ti^{3+} ions in the $M1$ site.

(d) Crystal Field States of Ti^{3+} and Fe^{2+} in a Distorted Coordination Site

The field-free Fe^{2+} and Ti^{3+} ions both have D spectroscopic ground terms, which give rise to T_{2g} ground states and E_g excited states when the ions are in octahedral coordination in an oxide or silicate structure (Figure 3). The electronic configuration of the Ti^{3+} ion, $[A]3d^1$, is particularly simple in an octahedral crystal field. The ground state configuration, $(t_{2g})^1(e_g)^0$, is three-fold degenerate and is designated $^2T_{2g}$. The single $3d$ electron is excited into an e_g orbital by visible radiation, giving the excited state configuration $(t_{2g})^0(e_g)^1$ which is doubly degenerate and is designated by ^2E_g. As a result of the dynamic Jahn-Teller effect (Cotton and Meyers, 1960), E_g excited states are resolved into two levels. Transitions to these levels produce asymmetric or two-peaked spectra in the visible region.

The crystal-field states are split further when the environment about the Ti^{3+} ions is distorted from octahedral symmetry. In low-symmetry environments, such as the clinopyroxene $M1$ site (Figure 2), the t_{2g} and e_g orbitals are resolved into a maximum of three and two energy levels, respectively (Figure 4). The representative spectral data of Ti(III) complexes summarized in Table 1 show typical splittings (α) for the e_g orbitals to be up to 4000 cm^{-1}. Splittings are smaller for the t_{2g} orbitals; magnetic data indicate β values (Figure 4) of up to 500 cm^{-1}. (Clark, 1968, p. 154).

The ground state configuration of Ti^{3+} corresponds to electron occupancy of the lowest energy t_{2g}-type orbital. Visible light excites this electron to each of the orbitals of the e_g-type orbital level, while transitions to the upper level produce the band at 21,000 cm^{-1} (Figure 4). The energy separation, 4,500 cm^{-1}, is thus a direct consequence of the splitting of the e_g-type orbitals of Ti^{3+} in the distorted $M1$ site. Note that the baricenter of the e_g levels of Ti^{3+} ions in the Allende pyroxene is approximately 18,750 cm^{-1} above the ground state (Figure 4), which is identical to that derived for Ti^{3+} in the Apollo 11 clinopyroxenes (Table 1).

The electronic configurations and crystal field states of Fe^{2+}, $3d^6$, are similar to Ti^{3+} (Figure 3). The quintet $^5T_{2g}$ state corresponds to the ground-state configuration $(t_{2g})^4(e_g)^2$. The sixth $3d$ elec-
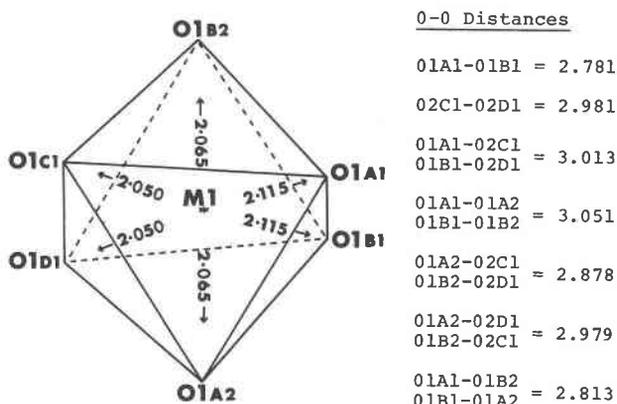

FIG. 2. (100) projection illustrating the distortion of the $M1$ coordination site in clinopyroxenes. Metal-oxygen and oxygen-oxygen distances are in Å. Data from Clark *et al* (1969).

0-0 Distances	
01A1-01B1	= 2.781
02C1-02D1	= 2.981
01A1-02C1 01B1-02D1	= 3.013
01A1-01A2 01B1-01B2	= 3.051
01A2-02C1 01B2-02D1	= 2.878
01A2-02D1 01B2-02C1	= 2.979
01A1-01B2 01B1-01A2	= 2.813

tron of Fe^{2+} occupying a t_{2g} orbital behaves like the single $3d$ electron of Ti^{3+}, giving rise to analogous absorption bands around 1000 nm in the near infrared region (Figure 1). The smaller energy separation (1000–1500 cm^{-1}) between the split e_g-type orbital energy levels of Fe^{2+} in diopside is due partly to the reduced distortion of the diopside $M1$ site compared to that in the titanian fassaite and partly to the lower charge on the Fe^{2+} ion.

In summary, double-band crystal field spectra are predicted and observed for both Fe^{2+} and Ti^{3+} in
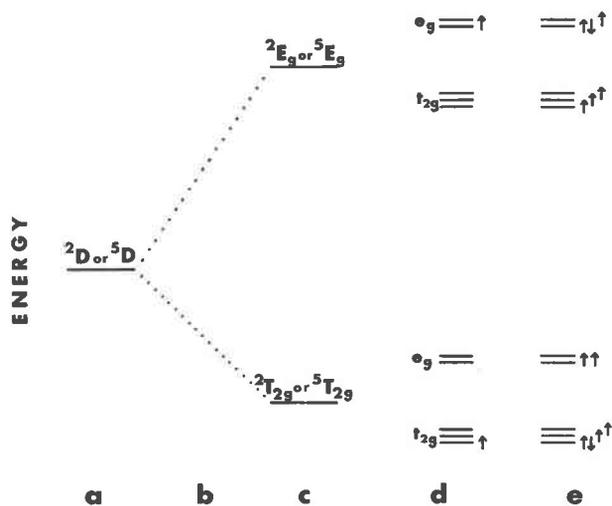

FIG. 3. Schematic energy level diagram for $Ti^{3+}(d^1)$ and $Fe^{2+}(d^6)$ in an octahedral crystal field. (a) Spectroscopic ground terms (b) Splitting of D terms in octahedral crystal field. (c) Crystal field states in octahedral coordination. (d) (e) Electronic configurations of the ground state and excited states of Ti^{3+} and Fe^{3+}, respectively.
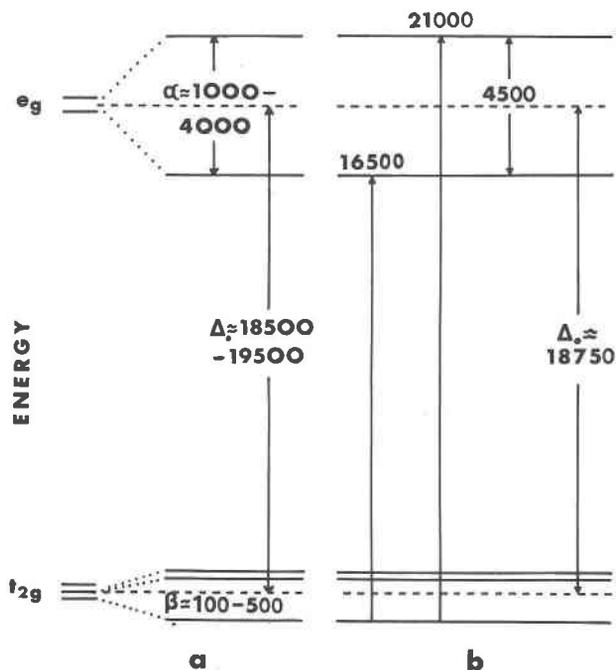
Fig. 4. Energy levels of $3d$ orbitals of Ti^{3+}. (a) Typical values for Ti(III) oxide compounds. (b) Values derived from absorption spectra of the titaniferous pyroxene in the Allende meteorite. All energies in cm^{-1} units.

distorted $M1$ sites of calcic clinopyroxenes. Thus, we believe that the bands at 21,000 cm^{-1} and 16,500 cm^{-1} reported by Dowty and Clark (1973) both represent crystal field transitions in Ti^{3+}.

(e) Positions of Absorption Bands in Relation to the Spectrochemical Series

The octahedral crystal field splitting parameter, Δ_o, for all transition metal ions depends on the type of anion or ligand coordinated to the cation. An abbreviated order of increasing Δ_o (that is, the spectrochemical series) is: halides < H_2O and oxides < NH_3 and amides < cyanides. Values of Δ_o are derived experimentally from positions of absorption bands. Examples for Ti(III) compounds are given in Table 1. Note that Δ_o for cyanide complexes is about 20,600 cm^{-1}, which exceeds the values for oxygen complexes by about 2000 cm^{-1}.

Dowty and Clark (1973) assign only the 21,000 cm^{-1} band in the spectrum of the Allende pyroxene to a crystal field transition in Ti^{3+} ions. This implies that Δ_o for Ti^{3+} in this pyroxene is approximately 21,000 cm^{-1} or higher, which exceeds the value for Ti(III) cyanide complexes. Clearly, this is at variance with trends shown in the spectrochemical series for other transition elements. If the band at 21,000

cm^{-1} in the Allende pyroxene is assigned to a crystal field transition in Ti^{3+}, then there *must* (group theoretical selection rules permitting) be a second crystal field band located at lower energy, such as 16,500 cm^{-1}, in order to lower the value of Δ_o to a value expected for Ti^{3+} coordinated to oxygen. Therefore, the spectrochemical series provides another argument in support of the assignment of the 16,500 cm^{-1} band in the Allende pyroxene to a crystal field transition in Ti^{3+} ions.

(f) Band Intensities for Metal-Metal Charge Transfer Transitions

Dowty and Clark (1973) argue from the polarization dependence of the band at 16,500 cm^{-1} that this band represents a charge transfer transition between Ti^{3+} and Ti^{4+} ions in the neighboring $M1$ positions of the Allende pyroxene. This assignment may be negated by reference to the Fe^{2+}–Fe^{3+} charge transfer band in hedenbergite (Fig. 1). The chemical analysis of the hedenbergite shows 25.78 percent FeO and 1.53 Fe_2O_3 (J. H. Scoon, personal communication, in Bancroft *et al*, 1967), giving a $Fe^{3+}:Fe^{2+}$ ratio of 1:20. In spite of the small proportion of Fe^{3+} ions, and therefore small probability of adjacent Fe^{2+}–Fe^{3+} ion pairs, the charge-transfer band around 12,000 cm^{-1} has an intensity comparable to that of the Fe^{2+} crystal field transition around 10,000 cm^{-1}. This conforms with group theory selection rules which predict greater probability of a charge transfer transition relative to a $d \rightarrow d$ crystal field transition. Note, also, that the charge transfer band in hedenbergite is not polarization dependent.

The chemical formula of the Allende fassaite derived by Dowty and Clark (1973) shows a $Ti^{4+}:Ti^{3+}$ ratio of approximately 2:7, indicating a considerably higher probability of Ti^{3+} and Ti^{4+} ion pairs in adjacent $M1$ positions than of Fe^{2+}–Fe^{3+} ion pairs in the hedenbergite. If the 16,500 cm^{-1} band were a Ti^{3+}–Ti^{4+} charge-transfer transition, its intensity would have to be considerably higher than the Ti^{3+} crystal field band proposed at 21,000 cm^{-1}. Furthermore, by analogy with the Fe^{2+}–Fe^{3+} charge transfer band in hedenbergite, the 16,500 cm^{-1} band should not show polarization dependence. However, by analogy with the crystal field spectra of Fe^{2+} ions shown in Figure 1, both the relative intensity and polarization dependence of the 16,500 cm^{-1} band of the Allende pyroxene may be readily explained as crystal field transitions in Ti^{3+} ions.

TABLE 1. Crystal Field Spectra of Ti(III) Compounds

Compound	Absorption Bands (cm^{-1})		Splitting of e_g levels, (cm^{-1})	Approx. Δ_o (cm^{-1})	References
$K_3Ti(CN)_6 \cdot 2KCN$	22,300	18,900	3,400	20,600	1
Ti^{3+}-doped Al_2O_3	20,300	18,450	1,850	19,375	2
$CsTi(SO_4)_2 \cdot 12H_2O$	19,900	18,000	1,900	18,950	3
$Ti(H_2O)_6Cl_3$	20,100	17,000	3,100	18,575	4
$(NH_4)_3[TiF_6]$	19,000	15,100	3,900	17,050	5
α-$TiCl_3$	13,800	12,000	1,800	12,900	6
Apollo 11 pyroxene (10047)	21,500	16,000	5,500	18,750	7
Allende fassaite	21,000	16,500	4,500	18,750	8
$NaTiSi_2O_6$	≈(22,000)*	15,600	≈(6,300)*	(18,750)*	9

* Inferred, see text.

1. H.L. Schläfer and R. Götz, Z. anorg. allgem. Chem., 309, 104 (1961).
2. D.S. McClure, J. Chem. Phys., 36, 2757 (1962).
3. H.L. Schläfer, Proc. Sump. Theory Struct. Complex Comp., Wroclaw, 1962 Pergamon, Press, p. 181.
4. H. Hartmann, H.L. Schläfer and K.H. Hansen, A. anorg. allgem. Chem., 284, 153 (1956).
5. H.D. Bedon, S.M. Horner and S.Y. Tyree, Inorg. Chem., 3, 647 (1964).
6. R.J.H. Clark, J. Chem. Soc., 417 (1964).
7. R.G. Burns, R.M. Abu-Eid and F.E. Huggins, Proc. 3rd Lunar Sci. Conf., Suppl. 3, vol. 1, 533–543 (1972).
8. E. Dowty and J.R. Clark, Amer. Min., 58, (1973).
9. C.T. Prewitt, R.D. Shannon and W.B. White, Contr. Mineral. Petrol., 35, 77 (1972).

Discussion

The arguments presented in the previous section not only demonstrate that two crystal-field absorption bands are to be expected for Ti^{3+} ions in distorted six-coordinate sites, but also invalidate the assignment of the band centered between 15,500–16,500 cm^{-1} in titaniferous pyroxenes to a Ti^{3+}–Ti^{4+} charge transfer transition. In support of their interpretation of the Allende fassaite spectra, Dowty and Clark (1973) cite diffuse reflectance spectral data for synthetic $NaTi^{3+}Si_2O_6$ (Prewitt *et al*, 1972). The spectrum illustrated by Prewitt *et al* (1972) shows a weak, broad band at 15,600 cm^{-1} and an intense absorption edge commencing around 500 nm (20,000 cm^{-1}) and obliterating the blue region of the spectrum. They interpreted the 15,600 cm^{-1} band as ". . . a charge transfer process between Ti^{3+} ions and some residual Ti^{4+} along the face-sharing[1]

[1] Presumably "edge-sharing $M1$ octahedral chains" is intended. Face sharing of octahedra does not occur in the pyroxene structure, in accord with Pauling's third rule.

$M1$ octahedral chains." No explanation was offered for the missing crystal-field features necessitated by the abundant Ti^{3+} ions in a stoichiometric $NaTi^{3+}Si_2O_6$ pyroxene, nor for how Ti^{4+} could be present in the $M1$ sites. To demonstrate that the 15,600 cm^{-1} band in the spectrum of synthetic $NaTiSi_2O_6$ is also a crystal-field transition in Ti^{3+} ions, we now cite structural data for several clinopyroxenes.

Selected interatomic distances for a variety of clinopyroxenes (Table 2) show for each structure a wide range of metal-oxygen and oxygen-oxygen distances in the coordination polyhedron about the $M1$ positions. This indicates considerable distortion of the $M1$ coordination sites from octahedral symmetry. Note that the larger distortion of the $M1$ site (based on ranges of $M1$–O distances) in acmite compared to that in ureyite appears to be correlated with the larger ionic radius of Fe^{3+} (0.645 Å) relative to Cr^{3+} (0.615 Å) for these transition-metal-bearing sodic pyroxenes. Although crystal structural data for synthetic $NaTi^{3+}Si_2O_6$ are not yet available (Prewitt, personal communication), the larger ionic

TABLE 2. Selected Bond Lengths in Certain Clinopyroxenes

Bond and {multiplicity}		Diopside $CaMgSi_2O_6$ (1)	Allende* Fassaite (2)	Jadeite $NaAlSi_2O_6$ (3)	Ureyite $NaCrSi_2O_6$ (4)	Acmite $NaFeSi_2O_6$ (5)
M1-O1A1,	B1 {2}	2.115	2.120	1.996	2.039	2.109
M1-O1A2,	B2 {2}	2.065	2.064	1.933	2.009	2.029
M1-O2lC1,	D1 {2}	2.050	1.993	1.856	1.947	1.936
Mean M1-O	{6}	2.077	2.059	1.928	1.998	2.025
Range		0.065	0.127	0.140	0.092	0.173
O1A1-O1B1		2.781	2.78	2.726	2.775	2.798
O2C1-O2D1		2.981	2.98	2.790	2.897	2.941
O1A1-O2C1	{2}	3.013	2.88	2.716	2.815	2.860
O1A1-O1A2	{2}	3.051	3.10	2.918	2.975	2.985
O1A2-O2Ci	{2}	2.878	2.76	2.677	2.797	2.819
O1A2-O2D1	{2}	2.979	2.91	2.818	2.904	2.964
O1A1-O1B2	{2}	2.813	2.75	2.458	2.617	2.639
Mean O-O	{12}	2.936	2.88	2.724	2.824	2.856
Range		0.270	0.35	0.460	0.358	0.346

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*  O-O distances calculated from data of Dowty and Clark (1973).

(1)  J.R. Clark, D.E. Appleman and J.J. Papike, Min. Soc. Amer., Spec. Pap.,
              2, 31 (1969).
(2)  E. Dowty and J.R. Clark, Amer. Min., 58   (1973).
(3)  C.T. Prewitt and C.W. Burnham, Amer. Min., 51, 956 (1966); J.R. Clark
              et al., loc. cit.
(4)  J.R. Clark et al., loc. cit.
(5)  J.R. Clark et al., loc. cit.
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radius of Ti^{3+} (0.67) and the trends shown by the data in Table 2 suggest that considerable distortion of the $M1$ coordination site from octahedral symmetry is to be expected in $NaTi^{3+}Si_2O_6$.

Therefore, the spectrum of $NaTiSi_2O_6$ should contain two absorption bands representing crystal field transitions in Ti^{3+}, one at 15,600 cm^{-1} and another at higher energy. Assuming the crystal field splitting parameter, Δ_o, to be comparable to the value 18,750 cm^{-1} derived for Ti^{3+} ions in the Allende and Apollo 11 pyroxenes (Figure 4 and Table 1), the high energy band would be predicted to lie at about 22,000 cm^{-1}. In this location it would be obscured by the intense absorption edge beyond 500 nm observed by Prewitt *et al* (1972).

The occurrence of Ti^{3+} ions in clinopyroxenes provides yet another example of the stabilizing influence of a distorted coordination site in a silicate structure on the crystal chemistry of certain transition metal ions (Burns, 1970, pp. 119–124). The importance of this site-distortion effect is demonstrated not only by the well documented fractionations of Fe^{2+} ions (which have an electronic configuration analogous to Ti^{3+}, Figure 3) into the most distorted sites of silicate minerals, but also by the occurrence of unstable cations such as Mn^{3+} and Cr^{2+} in epidotes and lunar olivines, respectively. By analogy, the distorted $M1$ coordination site of clinopyroxenes not only enhances the crystal field stabil-

ization energy of Ti^{3+}, but also leads to the fractionation of this relatively unstable cation into the clinopyroxene structure. Failure to take into account this relatively new principle of crystal chemistry inevitably leads to misinterpretation of experimental data, such as incorrect assignments of absorption bands in crystal-field spectra.

Note Added. Our discussion of the broad absorption band at 21,000 cm^{-1} in the Allende titanian fassaite should not be confused with interpretations of the sharper peak at 22,000 cm^{-1} observed in the absorption spectra of terrestrial titanaugites. Current work on the Mössbauer and absorption spectra of several terrestrial titanaugites suggests that the spectral feature found at 22,000 cm^{-1} is due to absorption by Fe^{3+} ions in octahedral *and* tetrahedral coordination in the pyroxene structure (Burns, Abu-Eid, and Leung, 1972).

Acknowledgments

References

BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Applications of the Mössbauer effect to silicate mineralogy. I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta,* **31,** 2219–2246.

BURNS, R. G. (1970) *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press.

——, R. M. ABU-EID, AND F. E. HUGGINS (1972) Crystal field spectra of lunar pyroxenes. *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3* (in press).

——, ——, AND IRENE S. LEUNG (1972) Titanaugites contain tetrahedral Fe^{3+} ions: A Mössbauer and electronic absorption study. *Geol. Soc. Amer. Abstr. Programs,* **4,** 463–464.

CHRISTENSEN, A. N., AND R. G. HAZELL (1967) The crystal structure of $NaIn(SiO_3)_2$. *Acta Chem. Scand.* **21,** 1425–1429.

CLARK, JOAN R., D. E. APPLEMAN, AND J. J. PAPIKE (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Amer. Spec. Pap.* **2,** 31–50.

CLARK, R. J. H. (1968) *The Chemistry of Titanium and Vanadium.* Elsevier Publishing Co.

COTTON, F. A., AND M. D. MEYERS (1960) Magnetic and spectral properties of the spin-free $3d^6$ systems Fe(II) and Co(III) in cobalt (III) hexafluoride ion: probable observation of dynamic Jahn-Teller effects. *J. Amer. Chem. Soc.* **82,** 5023–5026.

DOWTY, E., AND J. R. CLARK (1973) Crystal structure refinement and visible-region absorption spectra of a Ti^{3+} fassaite from the Allende meteorite. *Amer. Mineral.* **58,** 230–242.

FREED, R. L., AND D. R. PEACOR (1967) Refinement of the crystal structure of johannsenite. *Amer. Mineral.* **52,** 709–720.

HARTMANN, H., AND H. L. SCHLÄFER (1951) Uber die Lichtabsorption komplexer Ionen des dreiwertigen Titans. *Z. Phys. Chem.* **197,** 116–142.

——, ——, AND K. H. HANSEN (1957) Uber die Lichtabsorption von Dipolkomplexen des III-wertigen Titans vom $Typ[TiA_6]^{3+}$ mit A $=$ H_2O, CH_3OH, C_2H_5OH und $(NH_2)_2$ CO. *Z. anorg. allgem. Chem.* **289,** 40–65.

HOFF, G. R., AND C. H. BRUBAKER, JR. (1971) The preparation and characterization of some mixed-ligand complexes of titanium (III). *Inorg. Chem.* **10,** 2063–2066.

PEACOR, D. R. (1967) Refinement of the crystal structure of a pyroxene of formula $M_I M_{II}(Si_{1.5}Al_{0.5})O_6$. *Amer. Mineral.* **52,** 31–41.

PREWITT, C. T., AND C. W. BURNHAM (1966) The crystal structure of jadeite, $NaAlSi_2O_6$. *Amer. Mineral.* **51,** 956–975.

PREWITT, C. T., R. D. SHANNON, AND W. B. WHITE (1972) Synthesis of a pyroxene containing trivalent titanium. *Contrib. Mineral. Petrology* **35,** 77–82.

SCHLÄFER, H. L. (1964) Lichtabsorptionseigen-schafter und Magnetische Momente von oktaedrischen komplexverbindungen des III-Wertigen Titans. *In,* B. Jezowska-Trzebiatowska, Ed. "Theory and Structure of Complex Compounds," *Proc. Symp. Theory Struct. Complex Comp., Wroclaw, 1962,* pp. 181–193.

SCHROPFER, L. (1971) Uber den gekoppelten Ersatz von $Mg^{2+}Si^{4+}$ durch $Ti^{4+}Al^{3+}$ im Diopsid. *Neues Jahrb. Mineral. Abh.* **116,** 20–40.

WARREN, B. E., AND W. L. BRAGG (1928) The crystal structure of diopside, $CaMg(SiO_3)_2$. *Z. Kristallogr.* **69,** 168–193.