

Structural interpretation of polarized absorption spectra of the Al-Fe-Mn-Cr epidotes

By R. G. BURNS¹ and R. G. J. STRENS²

Department of Mineralogy and Petrology, Downing Place, Cambridge

[Read 9 June 1966]

Summary. Measurements have been made of the magnetic susceptibility and of the polarized absorption spectra of epidotes of the Al-Fe, Al-Fe-Mn, and Al-Cr series. Magnetic susceptibility measurements at room temperature by the Guoy method indicate that Fe³⁺, Mn³⁺, and Cr³⁺ are in 'high-spin' electronic states in the epidote structure, and the electronic transitions observed in the absorption spectra have been assigned on this basis. The polarized spectra, measured over the range 4000 to 22 000 Å by a polarizing microscope using a universal stage technique, showed each epidote group to be distinctly pleochroic. This pleochroism correlates with the presence of ions in distorted coordination sites.

Extinction coefficients of Fe³⁺ in epidote are higher than those for other Fe (III) compounds, indicating that Fe³⁺ ions occupy the non-centrosymmetric (Al, Fe) site. The low value (13200 cm⁻¹ at 0.155 Fe³⁺ and 12700 cm⁻¹ at 0.915 Fe³⁺) of the crystal-field splitting parameter, Δ , implies that the site is easily expanded to accommodate ions larger than Al³⁺. There is also evidence that increasing Fe³⁺ content causes distortion of the (Al,Fe)O₆ octahedron, suggesting a possible mechanism for the zoisite \rightleftharpoons clinozoisite transition.

The spectra of Al-Mn-Fe epidotes have been interpreted in terms of intense contributions from Mn³⁺ ions in the non-centrosymmetric (Al, Fe) site, and weak contributions from Mn³⁺ ions in the centrosymmetric AlOH site. Values of Δ vary from 13730 cm⁻¹ (0.082 Mn³⁺) to 13400 cm⁻¹ (0.747 Mn³⁺). Both (Al, Fe) and AlOH sites have strong tetragonal distortions ($c/a \sim 0.95$), leading to the observed large Jahn-Teller splitting of 12000 cm⁻¹.

The Al-Cr epidote spectra show weak absorption bands, attributed to Cr³⁺ ions in a centrosymmetric site of approximately orthorhombic symmetry (i.e. the AlO site). The value of Δ is about 16300 cm⁻¹.

Review of all available data on the distribution of Fe³⁺, Mn³⁺, and Cr³⁺ between the sites gives the following site preferences: Fe³⁺, Al > AlO > AlOH; Mn³⁺, Al \gg AlOH \gg AlO; Cr³⁺, AlO \gg Al, AlOH.

THIS paper presents the results of absorption spectra measurements on epidotes of the Al-Fe, Al-Fe-Mn and Al-Fe-Cr series (Strens, 1966) over the wavelength range 4000 to 22 000 Å. Absorption within this region is due mainly to electronic transitions between *d* orbital energy levels. The spectral data yield information on thermodynamic

¹ Present address: Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand.

² Present address: Department of Earth Sciences, The University, Leeds 2.

aspects of transition-metal geochemistry (Burns, Clark, and Fyfe, 1964; Burns, 1965; Burns and Fyfe, 1967) and provide detailed structural information. It is also the purpose of the paper to indicate the value of one of several spectroscopic methods available for the solution of mineralogical problems.

The only spectral measurements reported previously on epidotes are those of Grum-Grzhimailo *et al.* (1962) on an Al-Fe epidote of unstated composition. In this study the authors concluded that epidote contained Fe^{3+} in octahedral coordination.

Experimental methods

Polarized spectral measurements over the range 4000 to 22 000 Å were made by a microscope technique (Burns, 1966) in which a thin section (0.01 to 0.4 mm) cut from rock containing the epidote or from a single crystal, and mounted with Canada balsam, was placed on a three-axis universal stage mounted on a polarizing microscope. A suitable indicatrix axis was oriented E-W, and the microscope was then mounted in the sample beam of a Cary model 14 spectrophotometer. An identical microscope system holding a glass slide and Canada balsam was placed in the reference beam. The extinction angle of epidotes shows little variation with wavelength, and the spectra were run over the whole range without readjustment.

Spectral measurements were made on nine Al-Fe, six Al-Fe-Mn and one Al-Cr epidotes, the compositions and sources of which are listed in table I. All three polarized spectra, corresponding to light vibrating along the α -, β -, and γ -axes, were measured. Absorption bands and peaks in the Al-Fe epidote spectra were weak, and thick (0.3 mm) plates were used. By contrast, the Al-Fe-Mn epidote spectra contained intense peaks, and thinner (0.03 mm) sections were used.

Paramagnetic susceptibility measurements were made at 22° C using a Guoy balance, with ferrous ammonium sulphate as standard (Lewis and Figgis, 1960). All measurements were corrected for the diamagnetism of the material before calculating magnetic moments from bulk susceptibility data (table II).

The structure of epidote

The structure of monoclinic Al-Fe epidote was described by Ito (1950), Belov and Rumanova (1954), and Ito *et al.* (1954). It consists of chains of AlO_6 and $\text{AlO}_4(\text{OH})_2$ octahedra sharing edges, and stretched along the *b*-axis. The chains are linked by SiO_4 and Si_2O_7 groups, forming

TABLE I. Compositions of epidotes. UC refers to the collection number at Department of Geology and Geophysics, University of California, Berkeley, California. The King Island specimen was from Dr. G. Baker of Melbourne, the Dauphiné from Dr. Y. Seki, the Llano from Dr. S. E. Clabaugh (Strens, 1966, table I, no. 6), and the Chikla from Dr. S. A. Bilgrami (*ibid.*, no. 14)

Specimen number or locality	Fe ₂ O ₃ (wt. %)	Fe ³⁺ per formula unit	Specimen number or locality	Fe ₂ O ₃ (wt. %)	Fe ³⁺ per formula unit	Mn ₂ O ₃ (wt. %)	Mn ³⁺ per formula unit
UC 13 472	2.47	0.155	UC 13 607	10.25	0.620	1.35	0.082
UC 13 512	8.66	0.507	UC 13 608	10.32	0.624	2.00	0.122
King Island	11.78	0.712	Llano	11.80	0.713	4.60	0.280
UC 13 528	12.10	0.753	UC 13 611	5.50	0.332	10.25	0.625
UC 13 571	13.13	0.823	UC 13 612	5.19	0.314	11.85	0.722
UC 13 589	13.48	0.845	Chikla	11.20	0.677	12.75	0.747
UC 13 575	13.79	0.864					
Dauphiné	14.62	0.915					

5-membered rings, which are bound in turn by (Al,Fe) in 6-coordination and by Ca in two positions of 6- to 10-coordination. Two oxygens and two hydroxyls per unit cell are not bound to Si, but to the Al of the $(\text{AlO}_4)_n$ and $(\text{AlO}_3\text{OH})_n$ chains, so that the structural formula of epidote may be written:

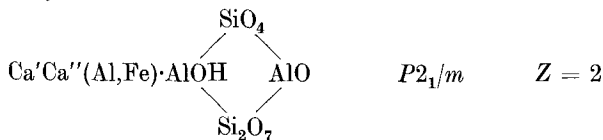


TABLE II. Magnetic susceptibility data for the epidote group

Specimen	Composition	Bulk magnetic susceptibility (10^6 cgs)	Molar magnetic susceptibility (10^6 cgs)	Diagmagnetic correction	Magnetic moment. (B.M.)
13 575	0.864 Fe^{3+}	31.1	14 870	181.5	5.99
13 611	0.625 Mn^{3+} 0.332 Fe^{3+}	8.92	15 830	180.5	4.96*

* Corrected for the molar magnetic susceptibility of Fe^{3+} : $14\,870 \times (0.332/0.864) \times 10^6 = 5720 \times 10^6$ cgs.

For convenience the three inequivalent sites will be denoted Al = (Al,Fe), AlOH = $(\text{AlO}_3\text{OH})_n$ chain site (Al₂ of Ito *et al.*, 1954), AlO = $(\text{AlO}_4)_n$ chain site (Al₁ of Ito *et al.*). The only significant replacements occurring in the minerals discussed in this paper are those of the three types of Al by M^{3+} ions of the first transition series, Fe^{3+} , Mn^{3+} , and Cr^{3+} . Only the coordination polyhedra about these ions will be considered in detail.

Descriptions of the octahedral sites. The (Al,Fe) O_6 group is non-centrosymmetric, with irregular metal-oxygen and oxygen-oxygen distances (fig. 1). Compression along the O_4 - O_8 axis gives an over-all tetragonal distortion ($c/a = 0.94$), modified by strong distortions of lower symmetry to give point and molecular symmetry of m (C_s).

The $\text{AlO}_4(\text{OH})_2$ group is compressed along the O_3 - O_3 axis, giving over-all tetragonal symmetry ($c/a = 0.95$), modified by slight monoclinic and minor triclinic components to give a point symmetry $\bar{1}$. The molecular symmetry approximates $4/mmm$ (D_{4h}).

The AlO_6 group is the most regular of the three, with all metal-oxygen distances equal, but there are slight orthorhombic and minor triclinic distortions giving a point symmetry $\bar{1}$. The molecular symmetry approximates $2/mmm$ (D_{2h}).

Relative energies of transition-metal d orbitals. In a regular octahedral site, a transition-metal ion is subjected to an electrostatic field (crystal

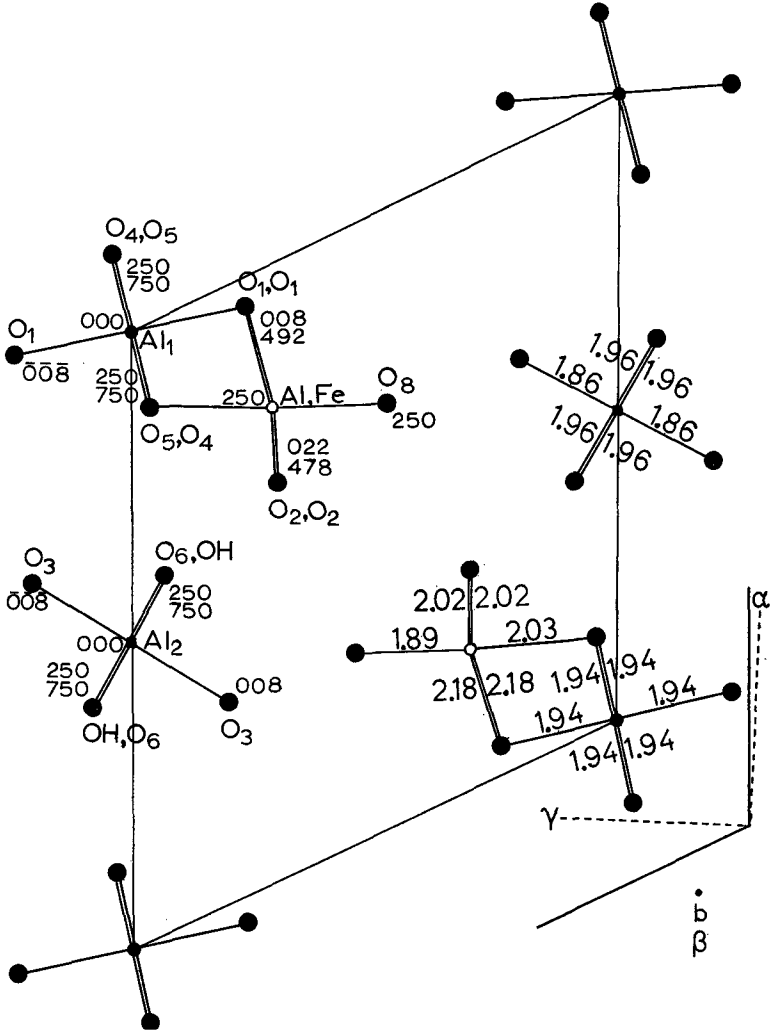


FIG. 1. Octahedral sites in the epidote structure in (010) projection with indicatrix axes shown: ● oxygen; ○ metal (III) ions.

field) originating in the anions, which splits the five d orbitals into two groups, separated by an energy Δ . The low-energy (t_{2g}) group consists of the three orbitals that project between the anions, whilst the high-energy (e_g) group consists of two orbitals projecting towards the anions. In distorted octahedra, such as those in epidote, the t_{2g} and e_g orbitals

are themselves resolved into different energy levels. All splittings obey a 'centre of gravity rule', i.e. the algebraic sum of the splittings is zero (fig. 2).

Absorption spectra of the Al-Fe epidotes

The polarized absorption spectra of an epidote containing 0.864 Fe^{3+} per formula unit are illustrated in fig. 3. The spectra consist of weak,

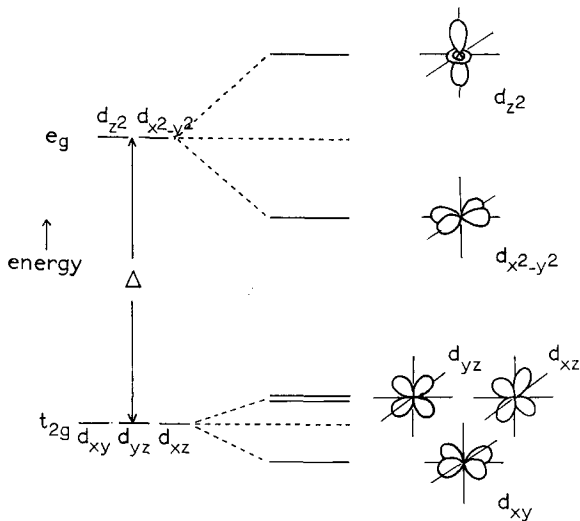


FIG. 2. Relative *d*-orbital energy-levels for a transition-metal ion in regular and tetragonally distorted ($c/a < 1$) octahedral coordination. The electronic *z*-axis (γ in epidote) is the axis of compression.

broad bands in the infra-red and visible regions, and sharp peaks in the violet that are situated on the shoulders of intense charge-transfer bands located in the ultra-violet.

Each polarized spectrum is distinctive. The α spectrum contains a weak band at 8400 \AA , a weak inflection at about 5600 \AA , and two sharp peaks at 4720 \AA and 4550 \AA . The β spectrum consists of two pronounced inflections at about 9000 \AA and 5600 \AA , and two sharp peaks at 4720 \AA and 4550 \AA . The γ spectrum has two well-defined bands at 10450 \AA and 6070 \AA , and two sharp peaks at 4720 \AA and 4550 \AA , the relative intensities of which differ from those of the corresponding peaks in the α and β spectra.

The spectra of other epidotes resemble those illustrated in fig. 3, and extinction coefficients of corresponding bands are approximately the

same. In low Fe^{3+} epidotes the two peaks between 4500 Å and 4750 Å are not resolved, but the peak at 4500 Å is asymmetric on the long wavelength side. The weak inflections in the α and β spectra become

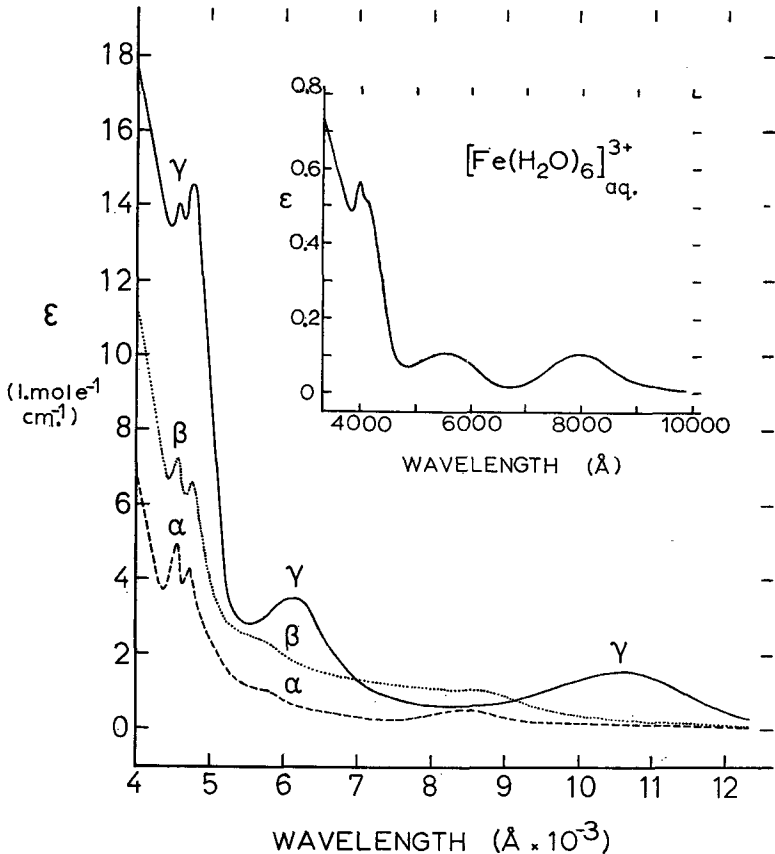


FIG. 3. Polarized absorption spectra of Al-Fe epidote containing 0.864 Fe^{3+} per formula unit, with the spectrum of aqueous Fe^{3+} (inset) for comparison.

inconspicuous but the broad bands in the α and γ spectra are still apparent in Fe^{3+} -poor epidotes. With increasing Fe^{3+} concentrations, absorption maxima of bands and peaks migrate, those at about 10 000 Å (γ spectrum), 6000 Å (γ spectrum), and 4500 Å (α , β , and γ spectra) to longer wavelengths, and the band at 9000 to 8300 Å (α spectrum) to shorter wavelengths. In addition, the band at about 4500 Å is resolved and migrates to longer wavelengths.

Interpretation of the spectra. The spectra of Al-Fe epidotes resemble those of other Fe (III) compounds (Jørgensen, 1954; 1962, p. 117). This feature is particularly noticeable in the γ spectra. However, the intensities of absorption bands in the epidote spectra are higher than those in other Fe(III) compounds (Jørgensen, 1954). This property, together with the pleochroic character of the spectra, indicates that the major contributions to the epidote spectra arise from Fe^{3+} ions in a non-centrosymmetric position in an anisotropic crystal-field such as that in the (Al,Fe) site. Constancy of the extinction coefficients over the whole range of Fe^{3+} concentration implies that contributions from Fe^{3+} ions in other positions, or from trace constituents such as Fe^{2+} and Mn^{2+} , are negligible.

The magnetic moment (5.99 B.M.) indicates that the electronic configuration of Fe^{3+} is one in which all five d orbitals are singly occupied with electron spins parallel. This would give rise to the sextet ${}^6A_{1g}$ ground state,¹ corresponding to the configuration $(t_{2g})^3(e_g)^2$ or $(d_{xz})^1(d_{xy})^1(d_{yz})^1(d_{x^2-y^2})^1(d_{z^2})^1$, if the Fe^{3+} ion was in an octahedral crystal-field. The ${}^6A_{1g}$ ground state is non-degenerate and resolution into states of lower degeneracy is not possible in crystal-fields of lower symmetry.

Excited states of Fe^{3+} in an octahedral crystal-field include the quartet states ${}^4T_{1g}$, ${}^4T_{2g}$, 4E_g , and ${}^4A_{1g}$, derived from the free-ion 4G state (fig. 4). These states correspond to electronic configurations with three unpaired electrons. The 4E_g , ${}^4A_{1g}$ doublet is frequently not resolved in octahedral crystal-fields. All transitions between the ${}^6A_{1g}$ ground-state and quartet excited states involve a reduction in the number of unpaired electrons, and are forbidden by the spin-multiplicity selection rule (Dunn, 1960). This condition is relaxed sufficiently by spin-orbit coupling for the transitions to have a low probability, resulting in the weak absorption bands observed in the Fe (III) spectra. The three bands generally observed correspond to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, and ${}^6A_{1g} \rightarrow {}^4A_{1g}$, 4E_g . The degenerate quartet states ${}^4T_{1g}$, ${}^4T_{2g}$, and 4E_g are resolved into states of lower degeneracy in a low symmetry crystal-field such as that within the (Al,Fe) site. As a

¹ Nomenclature of crystal-field states: A , B non-degenerate, respectively symmetrical and antisymmetrical with respect to the principal symmetry axis. E doubly degenerate; T triply degenerate; subscripts g , u symmetric and antisymmetric respectively under the operation of inversion through the centre of symmetry; subscript 1 refers to mirrorplanes \parallel to a symmetry axis; subscript 2 refers to diagonal mirror planes; superscript n refers to spin-multiplicities, where $n = 1$ plus number of unpaired electrons.

result, additional absorption bands are expected in the spectra of epidote relative to octahedral Fe(III) compounds.

The absorption bands at 10 450 Å (γ spectrum) and 8400–9000 Å (α and β spectra) represent transitions to the resolved components of the ${}^4T_{1g}$ state, whereas the bands at 6070 Å (γ spectrum) and 5600 Å (α and β spectra) correspond to transitions to components of the ${}^4T_{2g}$ state. The two peaks at 4720 and 4550 Å indicate that the apparent degeneracy of the ${}^4A_{1g}$, 4E_g doublet in an octahedral crystal-field is resolved in the epidote spectra. The peak at 4550 Å is attributed to the ${}^6A_{1g} \rightarrow {}^4A_{1g}$ transition, and the peak at 4720 Å represents a transition to a resolved component of the 4E_g state. The resolution of the ${}^4A_{1g}$, 4E_g doublet with increasing Fe³⁺ concentration is probably due to increased distortion of the (Al,Fe)O₆ group.

The crystal-field splitting parameter, Δ , may be estimated from the ${}^6A_{1g} \rightarrow {}^4A_{1g}$ energy separation, using the energy-level diagram constructed from Mn²⁺, $(t_{2g})^3(e_g)^2$, in an octahedral crystal-field. The diagram is applicable to Fe³⁺, $(t_{2g})^3(e_g)^2$, with a change of ordinate scale (Orgel, 1955). The ${}^6A_{1g} \rightarrow {}^4A_{1g}$ separation, calculated from the peak at 4550 Å in fig. 3, is 22 000 cm⁻¹. The energy of the unresolved ${}^4T_{1g}$ state, 10 730 cm⁻¹, is assumed to lie midway between the two components at 9570 cm⁻¹ (peak at 10 450 Å in the γ spectrum) and 11 900 cm⁻¹ (peak at 8400 Å in the α spectrum). Similarly, the energy of the unresolved ${}^4T_{2g}$ state, 17 170 cm⁻¹, is the mean of the two components at 16 480 cm⁻¹ (6070 Å in the γ spectrum) and 17 860 cm⁻¹ (5600 Å in the α and β spectra). These values lead to an estimated Δ of 12 750 ± 100 cm⁻¹ for the epidote with 0.864 Fe³⁺ (fig. 4). The value of Δ varies from 13 200 ± 100 cm⁻¹ to 12 700 ± 100 cm⁻¹ over the composition range 0.155 to 0.915 Fe³⁺. These values are lower than those for Fe(H₂O)₆³⁺, 13 700 cm⁻¹ (Orgel, 1960, p. 46), and iron yttrium garnet, 15 500 cm⁻¹ (Wickersheim and Lefever, 1962).

Absorption spectra of the Al-Fe-Mn epidotes

Polarized absorption spectra of a piemontite containing 0.625 Mn³⁺ are illustrated in fig. 5. The three polarized spectra are distinctive, and contain intense absorption bands in the visible and short-wave infra-red regions. The α spectrum contains an intense band at approximately 4500 Å and less intense bands at 5400 Å and 8000 Å. The β spectrum consists of intense bands at 4500 Å, 5600 Å, and 8300 Å. The γ spectrum has one intense band at 5500 Å, and a region of weak absorption around 8000 Å. The spectra are similar in each of the manganiferous epidotes

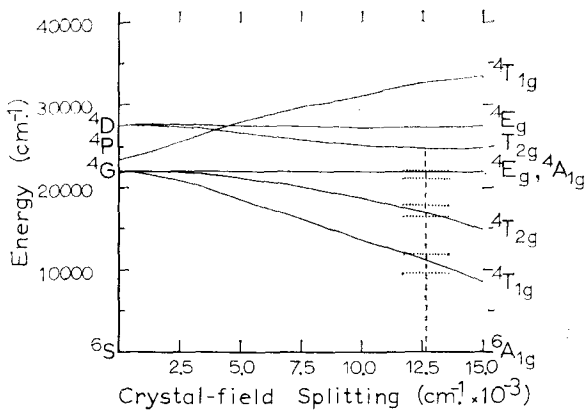


FIG. 4. Energy-level diagram for the Fe^{3+} ion in octahedral coordination, showing spectral transitions observed in epidote (fig. 3).

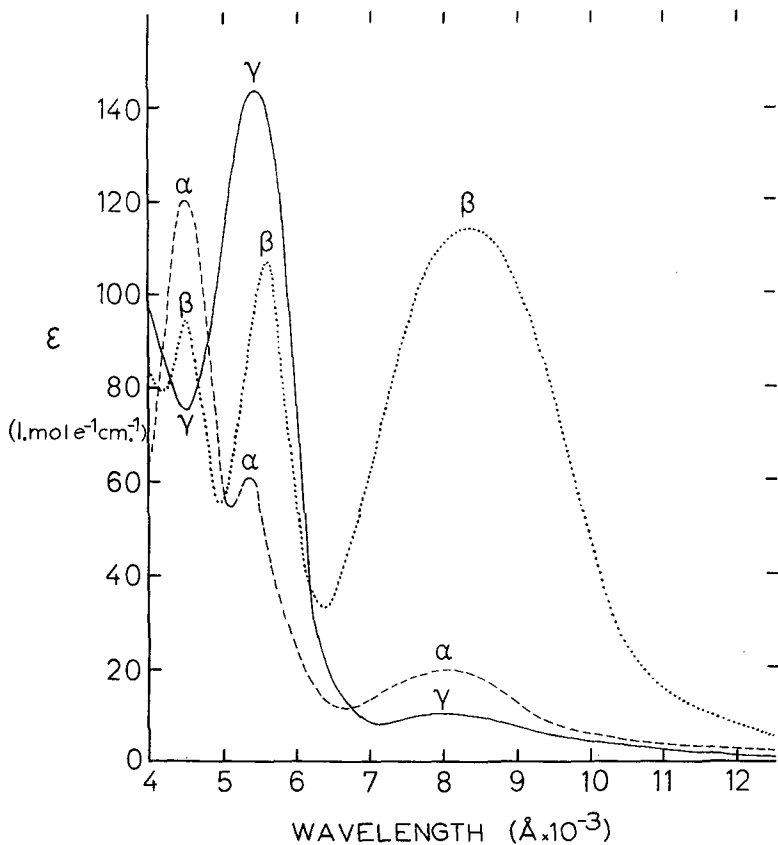


FIG. 5. Polarized absorption spectra of an Al-Mn-Fe epidote containing 0.625 Mn^{3+} and 0.332 Fe^{3+} per formula unit.

measured, except that intense absorption sets in below 5000 Å in specimens with high ($Mn^{3+} + Fe^{3+}$) concentrations, which tends to obscure the band at about 4500 Å in the β spectrum. Extinction coefficients

TABLE III. Wavelengths, wavenumbers, and extinction coefficients of absorption maxima in the polarized spectra of Al-Mn-Fe epidotes

Specimen number:	13 607	13 608	Llano	13 611	13 612	Chikla	
Composition:	Fe ³⁺ 0.620	0.624	0.713	0.332	0.314	0.677	
(M ³⁺ per formula unit)	Mn ³⁺ 0.082	0.122	0.280	0.625	0.722	0.747	
α spectrum:	Å	4420	4450	4420	4550	4550	4570
	cm ⁻¹	22 600	22 450	22 600	22 000	22 000	21 900
	ϵ	n.d.	162	n.d.	121	98	77
	Å	5340	5380	5400	5400	5350	5420
	cm ⁻¹	18 750	18 600	18 700	18 500	18 700	18 450
	ϵ	n.d.	92	n.d.	86	63	70
	Å	7900	7950	7950	7900	7950	8100
	cm ⁻¹	12 650	12 580	12 580	12 650	12 580	12 350
	ϵ	n.d.	46	n.d.	20	17	20
spectrum:	Å	4400	4400	4450	4450	4500	—
	cm ⁻¹	22 700	22 700	22 450	23 000	22 200	—
	ϵ	n.d.	123	n.d.	96	180	—
	Å	5520	5520	5570	5640	5620	5660
	cm ⁻¹	18 100	18 100	17 950	17 750	17 800	17 650
	ϵ	n.d.	172	n.d.	104	101	82
	Å	8200	8260	8240	8330	8400	8440
	cm ⁻¹	12 200	12 100	12 150	12 000	11 900	11 850
	ϵ	n.d.	137	n.d.	108	103	82
γ spectrum:	Å	5410	5410	5430	5480	5480	5550
	cm ⁻¹	18 500	18 500	18 400	18 250	18 250	18 000
	ϵ	n.d.	181	n.d.	142	99	81
Δ (cm ⁻¹)		13 730	13 700	13 690	13 450	13 550	13 400
	(cm ⁻¹)	14 340	14 270	14 290	14 060	14 080	13 960
CFSE* (Kcal per mole Mn ³⁺)		41.0	40.2	40.3	40.1	40.2	39.9

Note. ϵ , the molar extinction coefficient, is defined by $\epsilon = \{\log_{10}(I_0/I)\}/Ct$ where $\log_{10}(I_0/I)$ is the optical density measured experimentally, C is concentration of Mn^{3+} in moles per 1000 cc, and t is the thickness of the specimen in centimetres.

* Crystal-field stabilization energy.

of corresponding bands in the polarized spectra vary with composition (table III), and absorption maxima of all bands generally shift to longer wavelengths (smaller wavenumbers) with increasing Mn^{3+} concentration (fig. 6).

Since the sections used in the study of the Al-Fe-Mn epidotes were

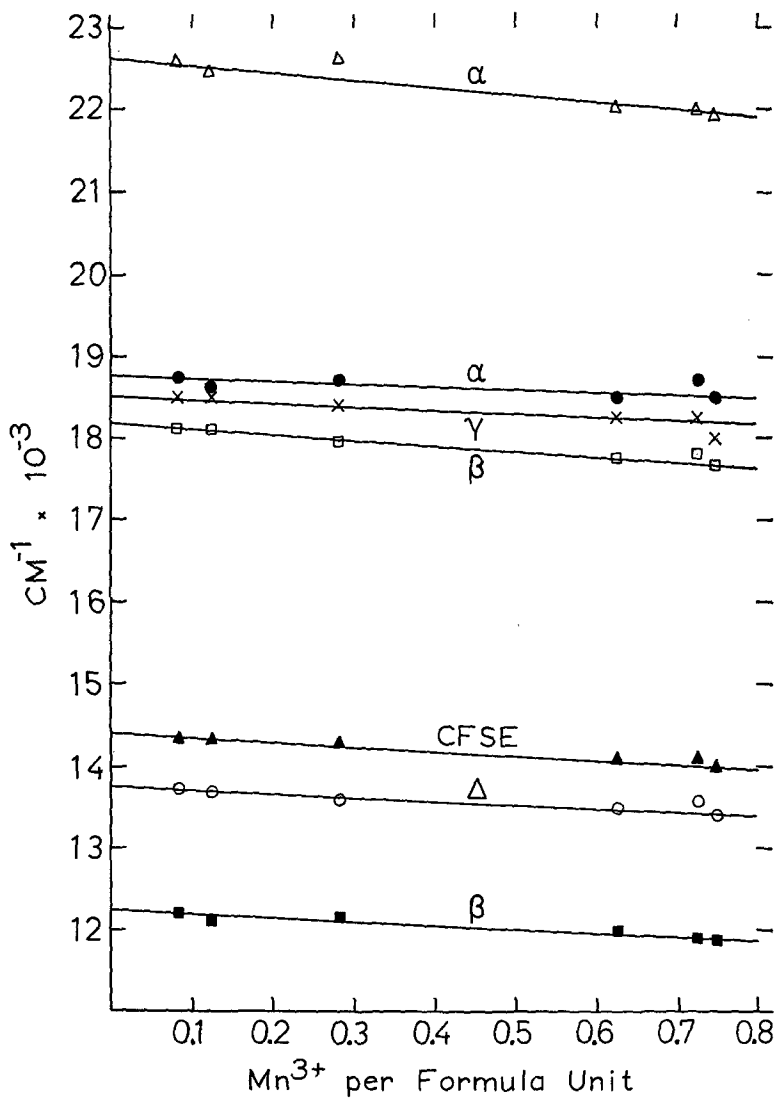


FIG. 6. Variation of peak maxima in α , β , and γ spectra, of crystal-field splitting (Δ), and of crystal-field stabilization energy (CFSE) with composition in Al-Mn-Fe epidotes. The CFSE is the sum of $3\Delta/5$ and half of the $d_{x^2-y^2}-d_{z^2}$ (or Jahn-Teller) splitting.

only one-tenth the thickness of those used for the Al-Fe epidotes, the weak, spin-forbidden transitions within the Fe^{3+} ion are not observed.

Interpretation of the spectra. The paramagnetic susceptibility measurements (table II; 4.96 B.M.) indicate that the Mn^{3+} ion has four unpaired electrons, which with Mn^{3+} in an octahedral field corresponds to the electronic configuration $(t_{2g})^3(e_g)^1$. This leads to a quintet 5E_g ground state. The only other quintet state is the threefold degenerate ${}^5T_{2g}$ excited state, corresponding to the configuration $(t_{2g})^2(e_g)^2$. One spin-allowed transition only is expected in an octahedral crystal-field. This is the ${}^5E_g \rightarrow {}^5T_{2g}$ transition involving electron transfer from one of the t_{2g} orbitals to the vacant e_g orbital.

The pronounced pleochroism displayed in the polarized spectra of Al-Mn-Fe epidote indicates that the observed transitions take place within Mn^{3+} ions in anisotropic crystal-fields such as those in the $(\text{Al,Fe})\text{O}_6$ and $\text{AlO}_4(\text{OH})_2$ polyhedra. Since both polyhedra are compressed along the z -electronic axis, the d_{z^2} orbital is highest in energy, and the $d_{x^2-y^2}$ orbital of the e_g group is occupied preferentially in the ground state of the Mn^{3+} ion. Spin-allowed transitions can thus occur between the d_{z^2} orbital and each of the singly occupied orbitals.

The symmetries of the crystal-fields in the $(\text{Al,Fe})\text{O}_6$ and $\text{AlO}_4(\text{OH})_2$ polyhedra are C_s and D_{4h} , respectively. In the centrosymmetric D_{4h} crystal-field, transitions that are allowed by the spin-multiplicity selection rule are forbidden by the Laporte selection rule (Dunn, 1960). Transitions have higher probability if the transition-metal ion does not lie at the centre of symmetry of its coordination polyhedron, and for D_{4h} symmetry transitions are aided by a vibronic coupling mechanism (Cotton, 1963, p. 231.). These lead to weak absorption bands, extinction coefficients of which are unlikely to exceed 15 (Dingle, 1965). The high intensities of the bands in the Al-Mn-Fe epidote spectra indicate that the major contribution is from Mn^{3+} ions in a non-centrosymmetric crystal-field such as that in the distorted $(\text{Al,Fe})\text{O}_6$ group. The variability of the extinction coefficients indicates the absorption is due to Mn^{3+} being present in more than one position.

The following assignments may be made to absorption bands in the polarized spectra. The band at about 8000 Å represents the $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, the band in the region 5400-5600 Å portrays the d_{xz} or $d_{yz} \rightarrow d_{z^2}$ transition, and the absorption band at 4500 Å, the $d_{xy} \rightarrow d_{z^2}$ transition.

A qualitative explanation for the polarization dependence of the

absorption bands is as follows. The probability of a transition is proportional to the integral

$$P \propto \int_{-\infty}^{+\infty} \psi_g \mu_x \psi_e dx,$$

where $\psi_g \psi_e$ are the wave-functions of the ground and excited states, respectively, and μ_x is the dipole moment component along x (Barrow, 1960, p. 72). In the spectra of Al-Mn-Fe epidotes, ψ_e is the d_{z^2} orbital. Transitions between the d_{xy} or $d_{x^2-y^2}$ and d_{z^2} orbitals lead to intense

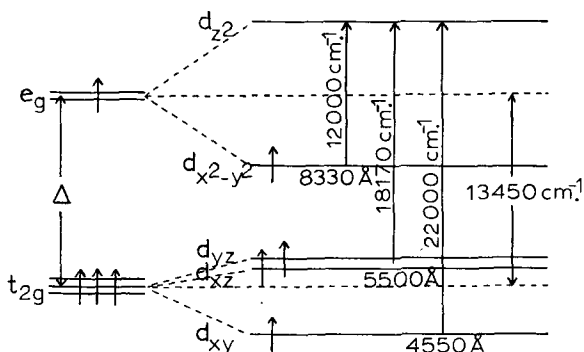


FIG. 7. Energy-level diagram for the Mn^{3+} ion in epidote, showing observed transitions (fig. 5).

absorption when radiation is polarized in the plane of the d_{xy} and $d_{x^2-y^2}$ orbitals (e.g. the bands at 4500 Å and 8000 Å in the α and β spectra), whereas transitions between the d_{yz} or d_{xz} and d_{z^2} orbitals lead to absorption when a component of the polarized radiation interacts with electrons in the d_{xz} or d_{yz} orbitals (e.g. the 5400–5600 Å peak in the α , β , and γ spectra).

The transitions are shown in fig. 7, together with the energy separations between d orbitals that have been deduced from the spectra. The energy separation, Δ , between unresolved t_{2g} and e_g orbital groups is calculated to be 13450 cm^{-1} . The values of Δ vary from 13 730 to 13 400 cm^{-1} over the composition range 0.082–0.747 Mn^{2+} per formula unit (fig. 6). These values compare with $\Delta = 13 100 cm^{-1}$ in viridine (Strens, unpublished data) and 21 000 cm^{-1} in caesium manganese (III) alum (Hartmann and Schläfer, 1951). The crystal-field stabilization energy of the Mn^{2+} ion in the (Al,Fe) site varies from 41.0 to 39.9 Kcal per gram ion (table III).

The increased absorption below 5000 Å in each polarized spectrum of piemontites in which the ($\text{Mn}^{3+} + \text{Fe}^{3+}$) ion concentration exceeds one per formula unit may be correlated with the entry of Mn^{3+} (and perhaps Fe^{3+}) into other positions of the epidote structure. The variable extinction coefficients (table III) also indicate that Mn^{3+} ions are not located entirely in the (Al,Fe) position but occupy the AlOH position as well. The $\text{AlO}_4(\text{OH})_2$ octahedron is compressed to approximately the same extent as the coordination polyhedron about the (Al,Fe) position, with the result that the $d_{xz-yz} \rightarrow d_{z^2}$ transition within Mn^{3+} in the two sites will absorb radiation at almost the same wavelength. Superposition of these two transitions contributes to the broadness of the band at 8000 Å. However, the average metal-oxygen distance in the AlOH site is lower than that in the (Al,Fe) site (fig. 1). Therefore, the $d_{xz}, d_{yz} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions will occur at shorter wavelengths within Mn^{3+} ions in the AlOH site, and also with reduced intensity, since the $\text{AlO}_4(\text{OH})_2$ group is centrosymmetric. Furthermore, both Δ and the crystal-field stabilization energy of the Mn^{3+} ion in the AlOH site should be larger than those for the (Al,Fe) site, but these could not be determined since the peaks could not be resolved.

Absorption spectra of Al-Cr epidote

The polarized spectra of a tawmawite containing 0.51 Cr^{3+} per formula unit are illustrated in fig. 8. Each spectrum consists of two moderately intense bands situated in the vicinity of 4000 Å and 6000 Å. Absorption maxima of corresponding bands occur at different wavelengths in the three polarized spectra.

Interpretation of the spectra. The Cr^{3+} ion has three unpaired electrons and possesses the electronic configuration $(t_{2g})^3(e_g)^0$ in an octahedral crystal-field. Two spin-allowed transitions are possible in the Cr^{3+} ion corresponding to excitation of one or two electrons into e_g orbitals. In ruby, for example, the $(t_{2g})^3 \rightarrow (t_{2g})^2(e_g)^1$ transition leads to absorption at about 5500 Å, and the transition $(t_{2g})^3 \rightarrow (t_{2g})^1(e_g)^2$ occurs at approximately 4050 Å (McClure, 1962). In low-symmetry crystal-fields the energy levels of the d orbitals constituting the t_{2g} and e_g orbital groups are resolved, and several transitions appear to be possible.

The small extinction coefficients of absorption bands in the tawmawite spectra indicate that transitions take place within Cr^{3+} ions located in a centrosymmetric coordination site such as the AlO_6 or $\text{AlO}_4(\text{OH})_2$ polyhedra of the epidote structure. The fact that absorption maxima corresponding to any one transition are located at different, but not

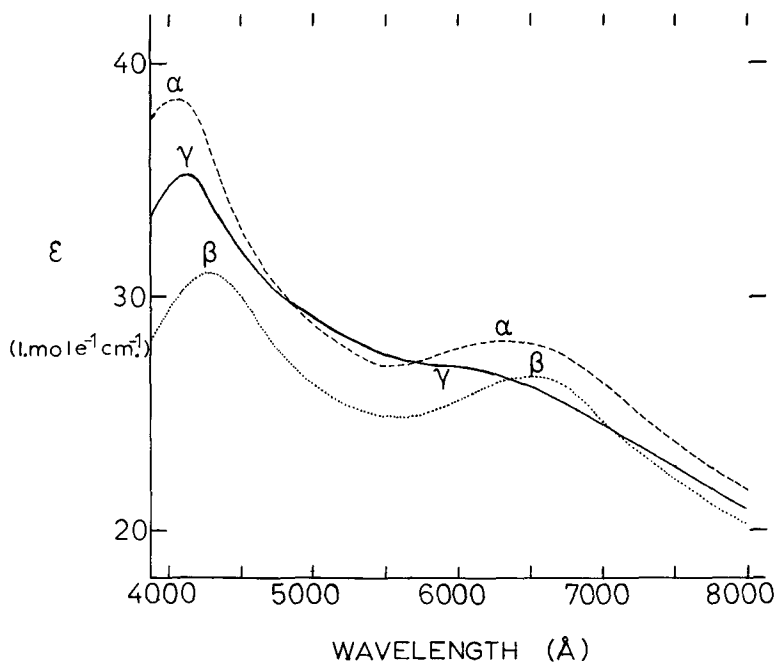


FIG. 8. Polarized absorption spectra of an Al-Cr epidote containing 0.51 Cr^{3+} per formula unit. Orientation, $\gamma = [010]$, $\alpha: [001] - 21^\circ$.

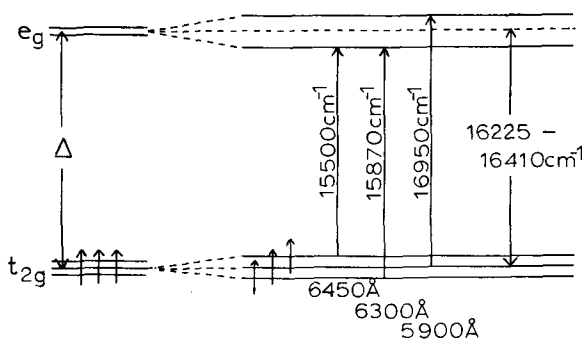


FIG. 9. Energy-level diagram for the Cr^{3+} ion in epidote, showing observed transitions (fig. 8)

widely separated, wavelengths in the three polarized spectra suggests that the Cr^{3+} ions occur in the symmetry D_{2h} crystal-field within the AlO_6 coordination site.

The following assignment of the absorption bands can be made. The bands at 6300 \AA or $15\,870 \text{ cm}^{-1}$ (α spectrum) and 6450 \AA or $15\,500 \text{ cm}^{-1}$ (β spectrum) represent transitions from resolved d orbitals of the t_{2g} group to the low-energy orbital of the resolved e_g group. The band at 5900 \AA or $16\,950 \text{ cm}^{-1}$ (γ spectrum) corresponds to a transition to the high-energy d orbital of the e_g group. The transitions are depicted in fig. 9, together with the d orbital energy separations deduced from the spectra. The crystal-field splitting, Δ , lies between $16\,220$ and $16\,410 \text{ cm}^{-1}$, the exact value depending on whether the transition observed at 5900 \AA or $16\,950 \text{ cm}^{-1}$ (γ spectrum) originates from the low- or high-energy d orbital of the resolved t_{2g} group. The value of Δ for Cr^{3+} in the epidote structure is smaller than those observed in other oxide structures, for example, in $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\Delta = 17\,400 \text{ cm}^{-1}$ (Orgel, 1960, p. 46), and for Cr^{3+} in corundum, $\Delta = 18\,150 \text{ cm}^{-1}$ (McClure, 1962). The crystal-field stabilization energy of the Cr^{3+} ion in the epidote structure, $6\Delta/5$, lies between 55.6 and 56.3 Kcal .

Applications of the spectral data

Calculation of metal-oxygen distances in epidotes. Detailed X-ray studies of Al-Cr and Al-Fe-Mn epidotes have not yet been made, and work on Al-Fe epidotes (Ito *et al.*, 1954) gives only the weighted mean (Al,Fe)-O distance in the Al site (2.05 \AA when occupied by approximately $0.15 \text{ Al} + 0.85 \text{ Fe}$), rather than the Fe-O distance. The spectra can be used to estimate actual distances in those sites partly occupied by Fe^{3+} , Mn^{3+} , and Cr^{3+} , rather than mean distances. The crystal-field splitting, Δ , varies approximately as the inverse fifth power of the mean metal-oxygen distance, $M\text{-O}$, so that $M\text{-O}$ may be found from the observed Δ if both $M\text{-O}$ and Δ are known for some standard oxygen compound of the same ion in a similar coordination.

In epidote with approximately 0.85 Fe^{3+} in the Al site, $\Delta = 12\,750 \text{ cm}^{-1}$, and in yttrium iron garnet $\Delta = 15\,500 \text{ cm}^{-1}$ (Wickersheim and Lefever, 1962). In the garnet $\text{Fe-O} = 2.012 \text{ \AA}$, hence Fe-O in epidote is 2.09 \AA for those sites occupied by Fe^{3+} compared with a radius sum $1.35 + 0.68 \text{ \AA} = 2.03 \text{ \AA}$. The slow decrease in Δ with increasing Fe^{3+} content probably reflects the overall expansion of the epidote structure to accommodate the larger Fe^{3+} ion.

In tawmawite with 0.51 Cr^{3+} , $\Delta = 16\,300 \text{ cm}^{-1}$, and in Cr_2O_3 , $\Delta =$

16 670 cm^{-1} (Neuhaus, 1960) and $\text{Cr-O} = 1.995 \text{ \AA}$ (Newnham and de Haan, 1962), from which Cr-O in tawmawite is 2.00 \AA , equal to the radius sum.

Standard values of Δ and Mn-O do not appear to exist at present, and the Mn-O distance in piemontite cannot be found. However, the splitting of the d_{z^2} and $d_{x^2-y^2}$ orbitals indicates that values in the xy plane will be larger than those along the $z(\gamma)$ axis, and will be in the ratio $c/a \leq 0.95$.

Substitution of Fe^{3+} , Mn^{3+} , and Cr^{3+} for Al. Inspection of available structural data suggests that Fe^{3+} replaces Al with relative ease when the Al-O distance exceeds the radius sum of 1.92 \AA . This is to be expected, since a shorter Al-O distance presumably indicates a 'tight' or compressed site, expanded only with difficulty to accommodate larger ions. Conversely, a 'loose' site with $\text{Al-O} \geq 1.92 \text{ \AA}$ should be easily expanded. For example, the solubility of Fe^{3+} in corundum (1.915 \AA), kyanite (1.897 to 1.915 \AA), and the chrysoberyl M_1 site (1.890 \AA) is very limited except at high temperature, whilst Fe^{3+} enters the epidote Al site (iron-free Al-O about 1.94 \AA), the chrysoberyl M_2 site (1.938 \AA), the grossular Al site (1.92 \AA) and to a smaller extent the epidote AlO site (1.93 \AA), and the andalusite chain site (1.935 \AA) at moderate temperatures. It appears, therefore, that values of Δ greater than those for $M(\text{H}_2\text{O})_6^{3+}$ indicate a 'tight' site; in the case of Fe^{3+} the division is at $13\,700 \text{ cm}^{-1}$.

Apart from considerations of size, which alone would be expected to limit substitution of Mn^{3+} for Al to those structures in which Fe^{3+} replaces Al readily, there is the additional condition that for Mn^{3+} to enter an octahedral site readily, that site should have either a pre-existing tetragonal distortion, or be easily distorted (Strens, 1965). For example, Mn^{3+} in the distorted Al and AlOH sites in epidote is stabilized by 17 Kcal/mole relative to Mn^{3+} in an undistorted octahedron. This condition is relaxed in the case of a dynamic Jahn-Teller effect (cf. manganese (III) acetylacetonate) and removed in the case of low-spin Mn^{3+} (t_{2g})⁴, both of which possibilities are unlikely in oxides.

Easy replacement of Al by Cr^{3+} should occur at moderate temperatures only in structures in which $\text{Al-O} = 1.92 \text{ \AA}$, and $\Delta \leq 17\,400 \text{ cm}^{-1}$, e.g. uvarovite, emerald, chrome-diopside, fuchsite (Neuhaus, 1960), and tawmawite. High Δ values for the Cr-poor end of a solid-solution series may imply limited solid solution, and possible existence of a solvus, as in the $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ series ($\Delta = 18\,000 \text{ cm}^{-1}$ in Al_2O_3 , $\Delta = 16\,670 \text{ cm}^{-1}$ in Cr_2O_3).

The zoisite \rightleftharpoons clinozoisite transition. It appears reasonable to suppose

that octahedral edges that are unshared or shared only with CaO_8 polyhedra (charge per oxygen, 0.25) will deform more easily on substitution of a large ion for Al than those shared with AlO_6 or SiO_4 polyhedra (charge per oxygen 0.5 and 1, respectively). Differential expansion along different octahedral edges could lead both to the resolution of the ${}^4A_{1g}$, 4E_g doublet, noted earlier, and to the zoisite \rightleftharpoons clinozoisite transition, which regularly occurs near 0.15 Fe^{3+} .

Use of M-O distances in estimating site populations. Average metal-oxygen distances have been used to estimate the degree of Al-Si replacement in the feldspars (Ferguson *et al.*, 1958), among other applications. Examples have been quoted above to show that Al-O varies significantly between different structures, and the wide range of Δ values recorded for certain transition-metal ions (e.g. Cr^{3+} , Neuhaus, 1960) points to the same conclusion, and indicates that site populations estimated from values of M-O might be seriously in error. The variation of Δ with Cr content in the Al_2O_3 - Cr_2O_3 series (Neuhaus, 1960) also indicates that the (Cr,Al)O distance may not vary linearly with composition.

Distribution of Fe^{3+} , Mn^{3+} , and Cr^{3+} between octahedral sites

Apart from the strong preference of Fe^{3+} for the Al site demonstrated by the structure determination, the site preferences of Fe^{3+} , Mn^{3+} , and Cr^{3+} in the epidote structure have not been determined with certainty. Although no one experimental approach gives the necessary information, analysis of all the data provided by crystal-field theory, X-ray work, optical properties, absorption spectra, and Mossbauer spectra does lead to a self-consistent set of preferences.

Crystal-field predictions. If other factors were constant spherically symmetrical Cr^{3+} and Fe^{3+} ions should marginally prefer undistorted octahedral sites, whilst the Mn^{3+} ion is stabilized in a tetragonally distorted octahedron (Jahn-Teller effect). Thus Mn^{3+} would be expected to enter the Al and AlOH sites in epidote, whilst Fe^{3+} and Cr^{3+} might possibly show a preference for the AlO site.

X-ray work. The work of Ito *et al.* (1954), Belov and Rumanova (1954), and Gottardi (1954) has shown that most of the iron in common epidote occupies the Al site. Six cycles of least-squares refinement, followed by difference Fourier syntheses, were carried out on Ito's published ($h0l$) intensity data for an epidote with 0.97 Fe^{3+} . Similar atomic coordinates were found to those originally obtained by Ito by hand computation. A distribution of the 0.97 Fe^{3+} near 0.87:0.10

between the Al and AlO sites gave the best results. Zero-layer *b*-axis Weissenberg photographs of piemontite, tawmawite, and iron-rich epidote made in the present study show no marked strengthening of the (00*l*), *l* even, reflexions relative to (00*l*), *l* odd, such as would occur if M^{3+} ions entered both chain sites. To the extent that Fe^{3+} , Mn^{3+} , and Cr^{3+} enter the chain sites, therefore, it is thought that one chain site is favoured in each case.

Optical properties. Arguments based on simple electrostatic theory (Strens, to be published) show that the optical orientation of compounds of ions with polarizabilities exceeding that of oxygen ($\alpha = 3.5$) depends mainly on distortions of the coordination polyhedra. Thus Fe^{3+} , Mn^{3+} , or Cr^{3+} ($\alpha \simeq 6$) entering the relatively undistorted AlO site would have little effect on the birefringence or, if the partial birefringences are not very small, on the extinction angle. Tawmawite has very low birefringence, which according to this theory would suggest that Cr^{3+} enters the AlO site. Similarly, the variation of γ and α : [001] (Strens, 1966) in the Al-Fe series would be consistent with entry of Fe^{3+} first into the Al site, and at high (≥ 0.85 Fe) iron contents into the AlO site. The variation in α : [001] and $\gamma - \alpha$ along the Al-Fe-Mn series is consistent with the entry of Mn^{3+} into the Al and AlOH sites, probably in that order.

Absorption spectra. The absorption spectra indicate that Fe^{3+} occupies a non-centrosymmetric octahedral site, i.e. the Al site, and that the Fe-O distance in this site is abnormally long. The spectrum of tawmawite with 0.51 Cr^{3+} indicates that Cr^{3+} occupies a centrosymmetric site with slight, probably orthorhombic, distortion, i.e. the AlO site. Spectra of piemontites show that Mn^{3+} occupies both a non-centrosymmetric tetragonally distorted site (Al), and a centrosymmetric tetragonally distorted site (AlOH) to a lesser degree.

Mössbauer spectra. The Mössbauer spectra of one Al-Fe-Mn and two Al-Fe epidotes (Bancroft and Burns, to be published) show a single unresolved peak consistent with the presence of high-spin Fe^{3+} in a distorted octahedral site.

Conclusions. The preceding data fall into a pattern consistent with the observed limits of solid solution in the various series, if the following site preferences are adopted: Fe^{3+} , Al > AlO > AlOH, (Fe^{3+} , 0-1.2); Mn^{3+} , Al \geq AlOH \gg AlO, (Mn^{3+} , 0-1.3, (Fe, Mn), 0-1.8); Cr^{3+} , AlO \gg Al, AlOH, (Cr^{3+} , 0-0.9, (Fe, Cr), 0-1.6).

Origins of colour and pleochroism. Colour is the response of the eye to radiation in the visible region of the electromagnetic spectrum (approximately 4000-7000 Å). The colour of epidotes, and many other silicate

minerals, is due to the presence of transition-metal ions in the structure. When the transition-metal ion occurs in a distorted coordination site, polarized radiation is absorbed to different degrees along different directions, leading to pleochroism.

The absorption spectra illustrated in figs. 3, 5, and 8 show that the Al-Fe-Mn-Cr epidotes exhibit pleochroism in both the visible and short-wave infra-red regions. In each case, the pleochroism is related to the presence of a transition-metal ion in an anisotropic electrostatic field within a distorted coordination site. Absorption of radiation in the visible region produces the complementary colours observed in polarized, transmitted light. The intensity of the colours may be correlated with intensity of absorption bands. Thus, Al-Fe epidotes exhibit pastel shades, the Al-Cr epidotes bright colours, and the Al-Mn-Fe epidotes vivid colours.

The positions of absorption bands determine the colours. Absorption of violet and blue dominate the spectra of Al-Fe epidotes, giving transmitted light its complementary yellow-green or yellow colour. The band in the yellow at about 6000 Å in the γ spectrum adds a complementary blue component, and produces transmitted light with a distinct greenish character. The band in the vicinity of 10 000 Å, however, is unlikely to have any optical effect. Thus, absorption of polarized light leads to the pleochroic scheme for Al-Fe epidotes: α pale yellow, β greenish yellow, γ yellowish green.

The pleochroic formula of Al-Mn-Fe epidotes: α lemon or orange-yellow, β amethyst, violet, or pink, γ bright red, may be explained by the polarized spectra as follows: The α spectrum is dominated by an intense absorption band in the blue, with a small contribution from a band in the green; transmitted light has the complementary yellow colour, which may be modified by the weaker band in the green to give an orange-yellow colour. The β spectrum shows absorption bands in the blue and yellow, and the shoulder of a broad, intense band in the near infrared at 8000 Å absorbs red radiation; the result is the complex amethyst or pink colour observed in transmitted light. The γ spectrum is dominated by the intense band in the green, with the result that transmitted light has the complementary bright red colour.

Absorption bands in the blue and violet dominate the spectra of the Al-Cr epidote, and yellow colours are to be anticipated. However, prominent absorption bands in the orange-red and the region of relatively lower absorption around 5500 Å in the α and β spectra produce green transmitted polarized light. This accounts for the pleochroic

formula of the tawmawite used in the present study: α and β emerald green, γ yellow.

Acknowledgements. We particularly wish to thank the many mineralogists, including S. O. Agrell, G. Baker, S. A. Bilgrami, S. E. Clabaugh, J. E. Dixon, W. S. Fyfe, C. O. Hutton, B. Lindqvist, K. J. Mills, A. Pabst, and Y. Seki who supplied epidote specimens for this work, and B. W. Evans for microprobe analyses of several samples. We also thank Mrs. V. M. Burns for editing and typing the manuscript. Thanks are due to the University of California Computer Center (Berkeley) for facilities and subsidized time, and the University Chemical Laboratories, Cambridge, for provision of research facilities.

The authors gratefully acknowledge financial support from the Royal Commission for the Exhibition of 1851, London, the University of New Zealand, and the University of California (R. G. B.); and from the University of Texas, the U.S. Office of Naval Research, and the U.K. Science Research Council (R. G. J. S.). Research grants from the National Science Foundation and Petroleum Research Fund of the American Chemical Society are also gratefully acknowledged.

References

- BARROW (G. M.), 1960. Introduction to Molecular Spectroscopy. McGraw-Hill Book Co., New York.
- [BELOV (N. V.) and RUMANOVA (I. M.)] БЕЛОВ (Н. В.) и Руманова (И. М.), 1954. Труды Инст. крист. Акад. наук СССР (Proc. Inst. Cryst. Acad. Sci. USSR), vol. 9, p. 103.
- BURNS (R. G.), 1965. Ph.D. Diss., Univ. California, Berkeley, California.
- 1966. Journ. Sci. Instr., vol. 43, p. 58.
- CLARK (R. H.), and FYFE (W. S.), 1964. Chemistry of the Earth's Crust. Proc. Vernadsky Cent. Symp., vol. 2, p. 88.
- and FYFE (W. S.), 1967, in ABELSON, (P.), ed., Researches in Geochemistry (J. Wiley and Sons, New York), second edn, (in press).
- COTTON, (F. A.), 1963. Chemical Applications of Group Theory. Interscience Publ., New York.
- DINGLE (R.), 1965. Inorg. Chem., vol. 4, p. 1287.
- DUNN (T. M.), 1960, in LEWIS (J.) and WILKINS, (R. G.), ed., Modern Coordination Chemistry (Interscience Publ., New York), p. 229.
- FERGUSON (R. B.), TRAILL (R. J.), and TAYLOR (W. H.), 1958. Acta Cryst., vol. 11, p. 331.
- GOTTARDI (G.), 1954. Periodico Min., vol. 23, p. 245.
- [GRUM-GRZHIMAILO (S. V.), BRILLIANTOV (N. A.), SVIRIDOV (D. T.), and SVIRIDOVA (R. K.)] Грум-Гржимайло (С. В.), Бриллиантов (Н. А.), Свиридов (Д. Т.), и Свиридова (Р. К.) 1963. Оптика и спектр., vol. 14, p. 228 (Optics and Spectr., vol. 14, p. 118).
- HARTMANN (H.) and SCHLÄFER (H. L.), 1951. Zeitschr. Naturforsch., vol. 6, p. 760.
- ITO (T.), 1950. X-ray Studies on Polymorphism. Maruzen Co., Tokyo.
- , MORIMOTO (N.), and SADANAGA (R.), 1954. Acta Cryst., vol. 7, p. 53.
- JØRGENSEN (C. K.), 1954. Acta Chem. Scand., vol. 8, p. 1502.
- 1962. Absorption Spectra and Chemical Bonding in Complexes (Pergamon Press, London).
- LEWIS (J.) and FIGGIS (B. N.), 1960, in LEWIS (J.) and WILKINS (R. G.), ed., Modern Coordination Chemistry (Interscience Publ., New York), p. 400.
- MCCLURE (D. S.), 1962. Journ. Chem. Phys., vol. 36, p. 2757.
- NEUHAUS (A.), 1960. Zeitschr. Krist., vol. 113, p. 195.

NEWNHAM (R. E.) and DE HAAN (Y. M.), 1962. *Zeitschr. Krist.*, vol. 117, p. 235.

ORTEL (L. E.), 1955. *Journ. Chem. Phys.*, vol. 23, p. 1004.

— 1960. *An Introduction to Transition-Metal Chemistry: Ligand-Field Theory* (Methuen and Co., London).

STRENS (R. G. J.), 1965. *Min. Mag.*, vol. 35, p. 547.

— 1966. *Ibid.*, vol. 35, p. 928.

WICKERSHEIM (K. A.) and LEFEVER (R. A.), 1962. *Journ. Chem. Phys.*, vol. 36, p. 844.

[*Manuscript received 28 September 1966*]
