A SPECTROSCOPIC INVESTIGATION OF MANGANIAN ANDALUSITE

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ABSTRACT

Polarized optical absorption spectra of natural manganian andalusite have revealed three intense absorption bands, at 14250, 22000 and 23500 cm^{-1}, assigned to spin-allowed d–d transitions in Mn^{3+} in the octahedral Al$_1$ sites. The crystal-field stabilization energy (CFSE) for Mn^{3+} in this position has been determined to be 47.6 kcal. Mössbauer spectra of manganian andalusite are dominated by one strong doublet with $\triangle_{298} = 1.73$-1.81 mm/s and $\delta_{298} = 0.35$-0.36 mm/s, caused by Fe^{3+} in the Al$_1$ position. The observed difference in $\triangle_{298}$ is due to the increasing distortion of the Al$_1$ sites when the amount of Mn^{3+} substituted for Al^{3+} is increased.

SOMMAIRE

Les spectres d'absorption optiques polarisés de l'andalousite manganifère naturelle ont révélé trois bandes d'absorption intenses, à 14250, 22000 et 23500 cm^{-1}, qui ont été assignées aux transitions d–d à spin permis dans Mn^{3+} dans les sites octa-édriques Al$_1$. L'énergie de stabilisation du champ cristallin, pour Mn^{3+} dans cette position, est de 47.6 kcal. Les spectres Mössbauer de l'andalousite manganifère sont caractérisés par un doublet intense, avec $\triangle_{298} = 1.73$–1.81 mm/s et $\delta_{298} = 0.35$–0.36 mm/s, qui est dû à Fe^{3+} dans la position Al$_1$. La différence observée dans $\triangle_{298}$ provient de la distorsion des sites Al$_1$ qui croît avec la quantité de Mn^{3+} substitué à Al^{3+}.

(Traduit par la Rédaction)

INTRODUCTION

Recently, Langer *et al.* (1976) presented polarized single-crystal spectra of a synthetic manganian andalusite. Earlier spectral data for natural manganian andalusites have been reported by Corin (1934) and Heinrich & Corey (1959). These data differ from those for synthetic manganian andalusite (Langer *et al.* 1976). To clarify this discrepancy, two natural manganian andalusites have been studied spectroscopically. The optical absorption spectra obtained in this study are shown to be in general agreement with those of synthetic Mn-andalusite. The color and pleochroism of iron- and titanium-bearing andalusites had previously been investigated by means of polarized optical absorption spectroscopy by Faye & Harris (1969).

CRYSTAL STRUCTURE

A structural refinement of andalusite was presented by Burnham & Buerger (1961). The structure consists of infinite Al–O octahedral chains parallel to the c axis formed by distorted octahedra that share edges. These chains are held together in the three-dimensional structure by isolated SiO$_4$ tetrahedra and dimers of edge-sharing, distorted AlO$_5$, trigonal bipyramids sharing corners with the Al–O octahedra (Fig. 1).

Aluminum atoms occur in two different positions: Al$_1$ in the highly distorted octahedral sites and Al$_2$ in the five-coordinated sites. The Al$_1$ atom is surrounded by six oxygen atoms, forming a distorted octahedron with point symmetry C_{2v}. As the deviation from a tetragonally-distorted octahedron with point symmetry D_{4h} is very small in this case, the Al$_1$ octahedron has been treated as a coordination site of that
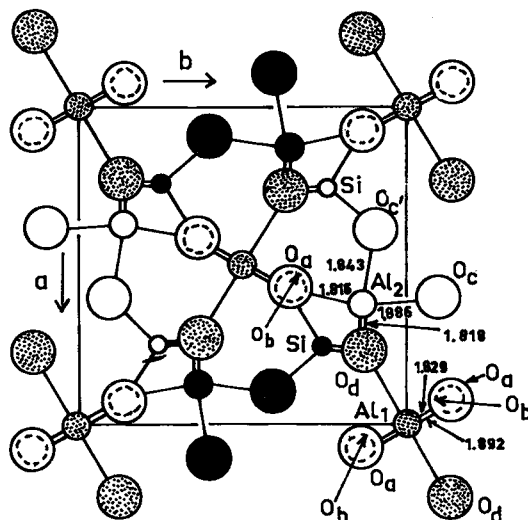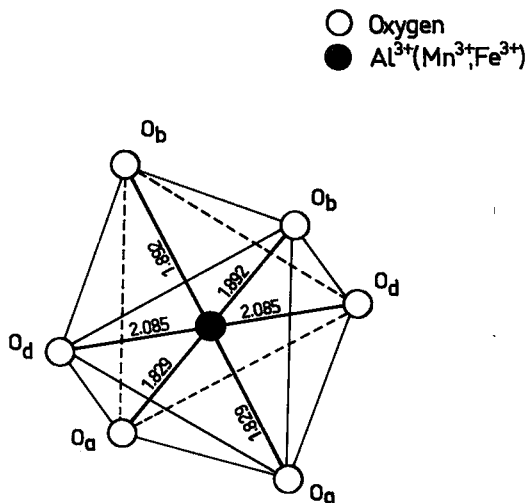

Fig. 1. Andalusite projection on (001) (data from Burnham & Buerger 1961). Solid circles: $z = 0$; dotted circles: $z \simeq \frac{1}{4}$; open circles: $z = \frac{1}{2}$.

○ Oxygen
● $Al^{3+}(Mn^{3+},Fe^{3+})$

$$c/a = \frac{2(Al_1 - O_d)}{(Al_1 - O_a) + (Al_1 - O_b)}$$

FIG. 2. The geometry of the Al_1 position in andalusite (data from Burnham & Buerger 1961).

symmetry when interpreting the spectral data (Fig. 2). The principal distortion from octahedral symmetry of these sites is one of elongation along one of the Cartesian axes $(O_d - Al_1 - O_d)$. This axis of distortion lies within the crystallographic plane a–b at an angle of 29.7° to the a axis. The average Al_1–O distance is 1.935Å and the difference between the largest and smallest Al_1–O distances is 0.256Å. Recent structural refinements of Mn-andalusites have shown that the Al_1 sites become more elongate when the amount of Mn^{3+} substituting for Al^{3+} increases, but the difference in bond length between the two Al_1–O bonds perpendicular to the O_d–Al_1–O_d axis is constant, i.e., 0.06Å (K. Langer, pers. comm.). This figure is valid for andalusites containing 17% or less of the hypothetical end-member Mn_2SiO_5. The average Al_2–O distance is 1.836Å and the maximum bond-length difference within the Al_2 octahedra is 0.070Å (Burnham & Buerger 1961).

INVESTIGATED SAMPLES

The two Mn-andalusites studied come from Ultevis and Västanå, Sweden. The Ultevis Mn-andalusite occurs in a metamorphosed quartzitic sedimentary rock (Ödman 1950). The mineral specimen was found in a coarse-grained part of

this rock type and here the andalusite crystals form clear green plates of maximum length 3 mm. The Mn-andalusite coexists with quartz, muscovite, K-feldspar and hematite. The Västanå andalusite occurs in a quartzitic mica schist (Bäckström 1896). The investigated sample was found in a disk-like concentration of small (0.2 mm or less in diameter) green grains of Mn-andalusite intermixed with subordinate amounts of quartz, pink muscovite and K-feldspar.

Chemical analyses of the two samples were performed by microprobe technique. The raw data were corrected by computer. The resulting microprobe analyses are reported in Table 1. Cr and Ti were below their detection limits of 0.02%. Cell parameters of the two samples were obtained by X-ray powder diffraction (Table 1). Calculations were carried out on four different reflections measured four times each, at a low goniometer speed (0.25° min⁻¹) and a high chart-speed. A Si internal standard was used.

EXPERIMENTAL

Mössbauer spectroscopy

Mineral powder suitable for Mössbauer transmission experiments was separated from crushed and sieved rock samples by repeated centrifugal separation in heavy liquids. These separated

TABLE 1.   COMPOSITION AND CELL PARAMETERS OF THE ANDALUSITES STUDIED

		Ultevis	Västanå
SiO_2	wt %	35.81	35.78
Al_2O_3		60.93	56.49
Fe_2O_3[+]		3.07	1.47
Mn_2O_3[++]		1.52	7.53
MgO		0.09	—
		101.42	101.27

Number of cations on the basis of 20 oxygens:

	Ultevis	Västanå
Si	3.88	3.94
Al	7.78	7.33
Fe^{3+}	0.25	0.12
Mn^{3+}	0.13	0.63
Mg	0.01	0.00
a (Å)	7.811 ±0.003	7.837 ±0.002
b (Å)	7.924 ±0.003	7.941 ±0.002
c (Å)	5.573 ±0.003	5.579± 0.002
V (Å³)	344.9 ±0.4	347.2 ± 0.3

+ Total iron as Fe_2O_3

++ Total manganese as Mn_2O_3

samples of Mn-andalusite were then hand-picked under a binocular microscope and analyzed by X-ray diffraction technique. They are believed to be at least 99% pure.

Mössbauer spectra were recorded by a constant acceleration system synchronized with a ND 512 MCA. The absorbers were Mn-andalusite powder mixed with boron nitride (BN) between mylar windows. Measurements were carried out with the absorbers kept at room temperature and at liquid-nitrogen temperature. The absorber density was 2.0 and 1.2 mg Fe/cm² for the Ultevis and Västanå samples, respectively. The transmitted radiation was detected by a Xe- and CO_2-filled proportional counter. As a source Co^{57} in Rh was used and the spectrometric velocities were calibrated against metallic iron.

The two mirror-symmetrical spectra obtained (256 channels each) were folded and fitted by computer technique, assuming absorption lines of Lorentzian shape.

Optical spectroscopy

Polarized optical absorption spectra of the Ultevis Mn-andalusite were obtained from two different absorbers. These consisted of two polished plates cut from a Mn-andalusite single crystal along two different crystallographic directions. Thus, one absorber was a α–β section of the mineral and the other absorber a β–γ section. As andalusite is orthorhombic, the three indicatrix axes are coincident with the crystallographic axes of the mineral. In each set the axes are mutually perpendicular. Mn-andalusite exhibits a good (110) cleavage and is markedly trichroic (Winchell & Winchell 1967). From these features, the two optical planes were determined. The absorbers prepared were examined microscopically and found to be correctly oriented to within $\pm 10°$.

Determination of the optical vibrational axes represented in the two absorbers was based on the pleochroic scheme of the Ultevis Mn-andalusites studied by Ödman (1950). In those andalusites, compositionally very similar to the one studied here, α is yellowish green, β grass green or emerald green and γ golden yellow or brownish yellow.

The grain size of the Mn-andalusite from Västanå was too small to allow single-crystal measurements and therefore only a powder spectrum, obtained in unpolarized light, was recorded.

All UV–VIS–NIR spectra were recorded with a Zeiss PMQ II single-beam spectrophotometer equipped with a photomultiplier and a PbS cell,

in the region 4000–26300cm⁻¹ at room temperature. In recording spectra of the Ultevis Mn-andalusite, plane-polarized light was obtained with a Nicol prism. In the region 600–4000 cm⁻¹ room-temperature spectra of powdered samples mixed with KBr were obtained with a Perkin-Elmer 279 IR spectrophotometer. The positions of band maxima and the intensities of the absorption bands were determined visually by assuming a Gaussian distribution of each band and by taking into account the background absorption and the possible overlapping of neighboring bands. Reported extinction coefficients are molar extinction coefficients (ϵ), calculated from the expression $\epsilon = A/\, t\, C$, where t is the thickness of the absorber in cm, C is the concentration of the absorbing species, *i.e.*, the concentration of the cation to which a certain absorption band is assigned, in moles per litre, and A is the net optical density *(OD)* at the band maximum. The unit of ϵ is litre/mole cm. The optical density is the experimentally measured quantity. C was calculated from the chemical analyses, assuming a density of 3.15 g/cm³ for andalusite.

TABLE 2. ⁵⁷Fe HYPERFINE PARAMETERS FOR ANDALUSITE

Sample	Temp. (°K)	Fe³⁺ Al₁ pos.			Fe³⁺ Al₂ pos.			Fe²⁺ Al₁ pos.		
		Δ	δ	I	Δ	δ	I	Δ	δ	I
Ultevis	298	1.73	0.35	82	1.17	0.12	11	1.95	1.02	7
	77	1.70	0.46	85	1.25	0.22	9	2.31	1.34	6
Västanå	298	1.81	0.36		not fitted					
	77	1.80	0.46		not fitted					

Δ = quadrupole splitting in mm sec⁻¹
δ = isomer shift relative to iron metal in mm sec⁻¹
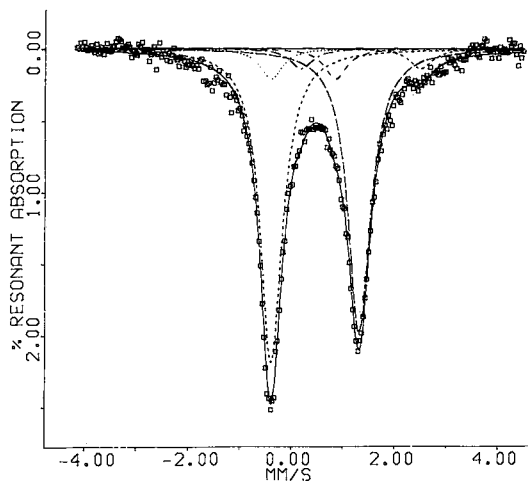I = given in percent of total absorption

FIG. 3. Mössbauer spectrum of the Ultevis Mn-andalusite at 77 K.

RESULTS

Mössbauer spectroscopy

The Mössbauer parameters obtained are summarized in Table 2 and a spectrum of the Ultevis Mn-andalusite at 77 K is shown in Figure 3. In the Ultevis spectra, three doublets were observed: an intense doublet with a small isomer shift and a large quadrupole splitting is assigned to Fe^{3+} in the Al_1 octahedron. A doublet with a smaller isomer shift is assigned to Fe^{3+} in the five-coordinated Al_2 sites. A third doublet with a large isomer shift and a large quadrupole splitting, increasing at low temperature, is assigned to Fe^{2+} in the Al_1 position. Similar assignments were proposed by F. Seifert (pers. comm.) for Fe doublets in a Mn-andalusite from Yakutia, USSR. Spectra of the Västanå Mn-andalusite were poorly resolved; only the intense doublet due to ferric iron in the Al_1 position could be accurately fitted. However, ferric iron could be seen in the five-coordinated Al_2 sites.

The isomer shifts observed for ferric and ferrous iron in the Al_1 position are characteristic of these ions in octahedral sites with oxygen ligands in silicates (Bancroft 1973). By analogy with the large quadrupole splitting observed for ferric iron in the distorted M_3 sites in allanite (Dollase 1971) the unusually large quadrupole splitting obtained for Fe^{3+} in Al_1 can be attributed to a large distortion from regular octahedral symmetry of these sites.

Isomer shifts for ferric iron have been shown to be correlated with cation–oxygen distances in coordination polyhedra in silicates in such a way that the isomer shift decreases when the average metal–oxygen distance decreases. In the light of this fact, the observed isomer shift for ferric iron in the Al_2 position is unexpectedly small. The average Al_2–O distance is 1.836Å and the observed isomer shift at room temperature is 0.12mm/s. These values should be compared with an isomer shift of 0.19mm/s observed for Fe^{3+} in tetrahedral sites in phlogopite (Hogarth et al. 1970), which has an average Al–O distance of 1.649Å only or with the isomer shift of 0.22mm/s for Fe^{3+} in tetrahedra in iron sanidine (Annersten 1976), which has an average Al–O distance of 1.662Å. The observed strong preference of Fe^{3+} for the octahedral Al_1 sites is in accordance with the results obtained from ESR measurements of andalusite (Holuj et al. 1966).
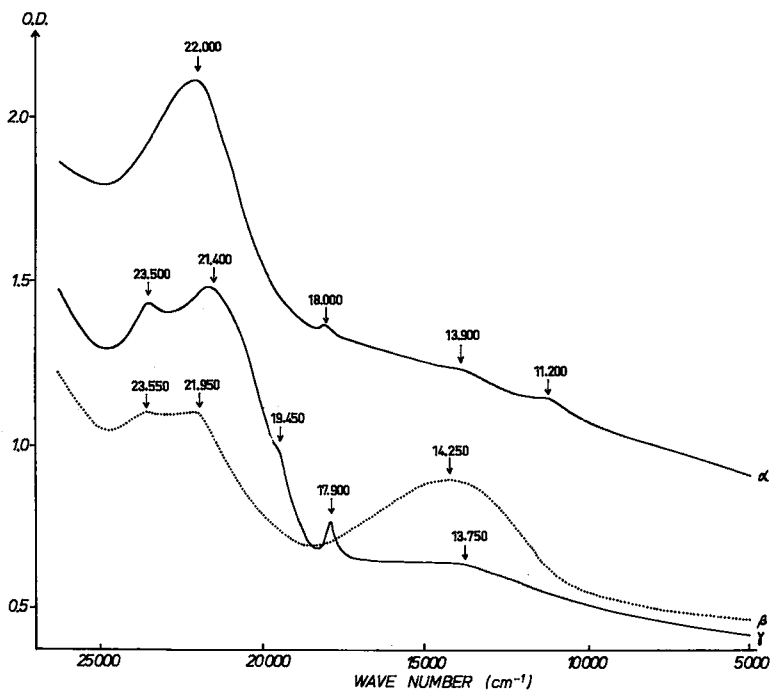

FIG. 4. Polarized absorption spectra of the Ultevis manganian andalusite. The dotted line is the β spectrum. Crystal thickness: 0.023 cm for the α spectrum and 0.016 cm for the β and γ spectra.

Optical spectroscopy

Polarized absorption spectra of the Ultevis Mn-andalusite (Fig. 4) are dominated by three intense bands at 14250, 22000 and 23500cm⁻¹. Additional weak absorption bands can be seen at 11200, 17900 and 19450cm⁻¹. In the unpolarized spectrum of the Västanå Mn-andalusite, only three bands can be observed, two moderately strong bands at 14500 and 22000 cm⁻¹ and a less intense band at 23550cm⁻¹. The full width at half maximum of the three intense bands is in the range of 1500–4000cm⁻¹ for both samples.

Comparing the spectra of the Mn-andalusites studied with the spectral data for the same mineral presented by Corin (1934) and Heinrich & Corey (1959), large differences are noted. Corin observed two absorption bands, one at 20000cm⁻¹ and another at 18200cm⁻¹. Heinrich & Corey found only one band centred at 18000cm⁻¹. On the other hand the present spectra are very similar to the polarized absorption spectra of a synthetic, pure Mn^{3+}-andalusite obtained by Langer *et al.* (1976). The Mn-andalusite that they studied had the composition $Al_{1.65}Mn^{3+}_{0.35}SiO_5$. They observed a moderately strong band at 22000cm⁻¹ and a weak band at 15800cm⁻¹ in the $E/\!/Y$ spectrum and a very strong band at 21900cm⁻¹, a weak band at 14900cm⁻¹ and a very weak and sharp band at 18180cm⁻¹ in the $E/\!/Z$ spectrum. No $E/\!/X$ spectrum was presented. In more recent studies of synthetic Mn^{3+}-andalusites a very weak band at 19800cm⁻¹ and a weak to moderately strong band at 29800cm⁻¹ have also been observed (K. Langer, pers. comm.).

In the spectra of iron- and titanium-bearing andalusites Faye & Harris (1969) observed five weak bands in the $E/\!/a$ spectrum. These bands at 14500, 22100, 23000, 24600 and 25200cm⁻¹ were assigned to spin-forbidden transitions in Fe^{3+} in the octahedral Al_1 sites. In the $E/\!/c$ spectrum they observed an intense and broad band centred at 20800cm⁻¹. This band was assigned to Ti^{3+}–Ti^{4+} charge transfer between ions in the chains of octahedra that extend along the c axis.

INTERPRETATION OF THE OPTICAL SPECTRA

Assignments of the absorption bands in the spectra of the Ultevis Mn-andalusite (Table 3) have been made under two major assumptions. Firstly, it has been assumed that Fe^{2+} and Mn^{2+} do not enter the andalusite structure in significant amounts, owing to the differences in ionic size and difficulties in compensating for valence differences when these ions substitute for Al^{3+}. It can be seen from the Mössbauer

TABLE 3. OBSERVED ABSORPTION BANDS DUE TO Mn^{3+}_{VI} IN THE ULTEVIS ANDALUSITE

Orientation	Band Position	ε Value[†]	Transition
α spectrum	22000 cm⁻¹	40	$^5B_{1g} \rightarrow {}^5B_{2g}$
	18000	2	$^5B_{1g} \rightarrow {}^3H$
	13900	1	$^5B_{1g} \rightarrow {}^5A_{1g}$
	11200	1	$^5B_{1g} \rightarrow {}^1I$
β spectrum	23550	10	$^5B_{1g} \rightarrow {}^5E_g$
	21950	25	$^5B_{1g} \rightarrow {}^5B_{2g}$
	14250	40	$^5B_{1g} \rightarrow {}^5A_{1g}$
γ spectrum	23500	20	$^5B_{1g} \rightarrow {}^5E_g$
	21400	60	$^5B_{1g} \rightarrow {}^5B_{2g}$
	19450	6	$^5B_{1g} \rightarrow {}^3H$
	17900	9	$^5B_{1g} \rightarrow {}^3H$
	13750	6	$^5B_{1g} \rightarrow {}^5A_{1g}$

[†] (1/mole cm).

data for the present samples (Table 2) that this assumption is valid at least for Fe^{2+}, and there is no reason to believe that Mn^{2+} should be more stabilized in the andalusite structure than Fe^{2+}. Actually, in an ESR spectrum of the Ultevis Mn-andalusite no lines caused by Mn^{2+} could be detected. Secondly, it has been assumed that the Al_1 position, which has a C_{2v} point symmetry, may be approximated by an octahedron with D_{4h} point symmetry, with an elongation of one of its Cartesian axes (O_d–Al_1–O_d). It can be seen from Figure 2 that the deviation from such a symmetry is very small in the present case.

High-spin Mn^{3+}, having a $3d^4$ configuration, is predicted by crystal-field theory to have three spin-allowed d-d transitions when found in a distorted octahedron with D_{4h} symmetry. In the case of the Al_1 octahedron in andalusite, in which the major distortion from O_h symmetry is one of elongation, the transitions between the split ^5D states should be $^5B_{1g}{\rightarrow}^5A_{1g}$, $^5B_{1g}{\rightarrow}^5B_{2g}$, $^5B_{1g}{\rightarrow}^5E_g$.

Mössbauer data for the present samples (Table 2) show that there exists a strong preference of Fe^{3+} for the Al_1 sites in andalusite. It is believed that Mn^{3+} is subject to the same behavior, owing to its large octahedral site-preference (Orgel 1966). Thus, it is reasonable to expect a maximum of three absorption bands due to spin-allowed d-d transitions in Mn^{3+} in the spectra of Mn-andalusites. Furthermore, these bands should dominate the optical spectra of the present Mn-andalusites, as Mn^{3+} is the only transition metal ion with spin-allowed transitions that is present in significant amounts in these samples.

The two more intense bands observed in the present spectra, at 22000 and 14250cm⁻¹, are

located at almost the same wave numbers as the two intense bands in spectra of a synthetic, pure Mn^{3+}–andalusite (Langer *et al.* 1976), and they show the same kind of polarization behavior. These two bands are assigned to spin-allowed transitions in Mn^{3+} in Al_1 sites in andalusite. The position of the third band is not obvious.

The transition representing the lowest energy in the present case is the $^5B_{1g}{\rightarrow}^5A_{1g}$. The $^5B_{1g}$ state corresponds here to a $3d$ electronic configuration, in which there is a hole in the $d_{x^2-y^2}$ orbital in an otherwise half-filled sub-shell, whereas the $^5A_{1g}$ state corresponds to a configuration where there is a hole in the d_{z^2} orbital. It has been shown that the energy separation between the d_{z^2} and the $d_{x^2-y^2}$ orbitals is considerably larger than the energy separation of the t_{2g} orbitals of a $3d$ ion in a tetragonally-distorted octahedron (Wood & Strens 1972). The energy difference between the two e_g orbitals is also sensitive to small changes in the c/a ratio of the octahedron in which the 3d ion is incorporated. The deviation of this ratio from 1.0 is a good estimate of the degree of tetragonal distortion to which the octahedron is subjected. Furthermore, Burns & Strens (1967) have assigned an absorption band near 12000 cm^{-1} in spectra of piemontite to the transition between $^5A_{1g}(D)$ and $^5B_{1g}(D)$ states in Mn^{3+} in M_3 sites in that mineral. That octahedral position has formal symmetry C_s (Dollase 1969), but its principal distortion from O_h symmetry is a tetragonal compression along one of its Cartesian axes. The tetragonal distortion of the M_3 sites in piemontite ($c/a \sim 0.95$) is somewhat smaller than for the Al_1 sites in andalusite ($c/a \sim 1.12$). Moreover, in the region 600–4000 cm^{-1} IR spectra for the present samples reveal only bands due to vibrational transitions in the region 600–1200 cm^{-1}. The bands are also observed in IR spectra of pure andalusites (Tarte 1963). Considering these observations it seems reasonable to suggest that the 14250cm^{-1} band in spectra of Mn-andalusite marks the $^5B_{1g}(D){\rightarrow}^5A_{1g}(D)$ transitions in Mn^{3+} in Al_1. Moreover, it has been shown by structural refinements of andalusite that the tetragonal distortion of the Al_1 sites increases with increasing substitution of Mn^{3+} for Al^{3+} in the mineral (K. Langer, pers. comm.). The c/a ratio of the Al_1 sites in pure andalusite is ~ 1.12 whereas in a Mn^{3+}-andalusite of composition $Al_{1.66}Mn_{0.34}SiO_5$, the ratio is ~ 1.16 (K. Langer, pers. comm.). When comparing the spectra of the Ultevis sample with those of an andalusite with higher Mn^{3+} content (Langer *et al.* 1976) one observes a shift of the 14250cm^{-1} band towards higher energies. This shift is also observed in the present spectra of the Västanå sample, richer in Mn, consistent with an assignment of this absorption band to the transition between the split ^5D states $^5B_{1g}$ and $^5A_{1g}$ in Mn^{3+} in the Al_1 position.

Thus, the two absorption bands due to the $^5B_{1g}{\rightarrow}^5B_{2g}$ and $^5B_{1g}{\rightarrow}^5E_g$ transitions in Mn^{3+} in the Al_1 position are expected at wave numbers higher than 14250cm^{-1}. The band at 22000cm^{-1}, already attributed to Mn^{3+} in the Al_1 sites, is assigned to the $^5B_{1g}{\rightarrow}^5B_{2g}$ transition, as no intense absorption band is present between 14250 and 22000cm^{-1}. The high-energy transition $^5B_{1g}{\rightarrow}^5E_g$ in Mn^{3+} in Al_1 is then expected to give rise to an absorption band at a wave number higher than 22000cm^{-1}. Considering the Mn^{3+} content in the present sample there is only one band in the spectra of the Mn-andalusite from Ultevis that is of sufficient intensity to be assigned to a spin-allowed d-d transition in that ion. That band is centred at 23500cm^{-1}. However, no intense absorption band at that wave number has been observed in the spectra of synthetic Mn^{3+}-andalusite, but it might be possible that there is a component of lower intensity at 23500cm^{-1} hidden under the envelope of the very intense band observed at 22000cm^{-1} in these spectra (K. Langer, pers. comm.). However, in more recently-obtained polarized absorption spectra of synthetic Mn^{3+}-andalusite a weak to moderately strong band at 29800cm^{-1} has been observed. This band was preferentially assigned to the $^5B_{1g}{\rightarrow}^5E_g$ transition in octahedrally bonded Mn^{3+} in andalusite (K. Langer, pers. comm.). If this assignment is correct the band at 23500cm^{-1} may be assigned to a spin-forbidden transition in ferric iron in the Al_1 position.

On basis of the chemical analysis and the Mössbauer data of the Ultevis Mn-andalusite the concentration of Fe^{3+}_{VI} in the sample can be calculated to be ~ 1.0 mole/l. This figure and the intensity of the band at 23500cm^{-1} yield an ϵ value of 9 if caused by Fe^{3+} in the Al_1 position. Faye & Harris (1969) observed two absorption bands, at 23000 and 22000cm^{-1} in their spectra of essentially Mn-free, iron- and titanium-bearing andalusites. They assigned these two bands to the field-independent $^6A_1{\rightarrow}^4A_1\ ^4E(G)$ transition in Fe^{3+} in the Al_1 sites in andalusite. However, the ϵ values of these two bands were reported to be 0.5–1.0 (Manning 1973). It should be noted, though, that the ϵ value for an absorption band caused by the $^6A_1{\rightarrow}^4A_1\ ^4E(G)$ transition in octahedrally-bonded ferric iron is expected to increase when the local environment around this ion is changed in such a way that the number of M^{3+} second-
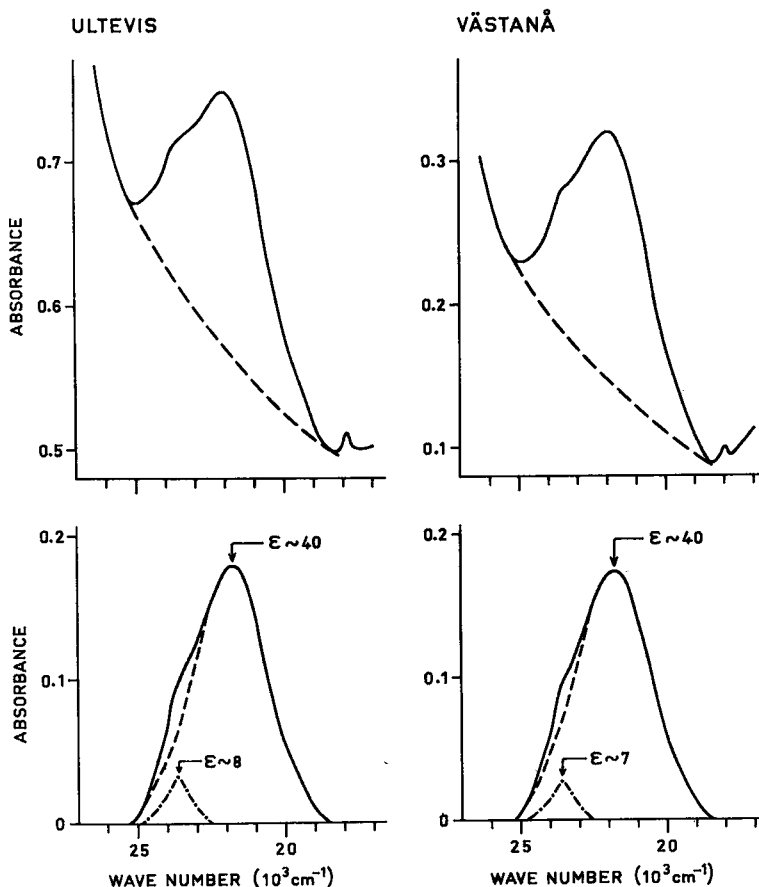
FIG. 5. Unpolarized spectra of the investigated samples in the region 17000–26300cm^{-1} and resolved components of the net absorption (lower spectra); ϵ values are calculated assuming Mn^{3+} as the absorbing species.

nearest neighbors is increased (Manning 1973). M^{3+} here represents octahedrally-bonded trivalent transition-metal ions. However, the ratio Mn^{3+} / Fe^{3+} is 10 times larger for the Västanå Mn-andalusite than in the Ultevis sample, but the ratio of the optical densities for the bands at 23500 and 22000cm^{-1} is nearly constant for the two samples at 1:6 (Fig. 5). Only an extensive clustering of M^{3+} ions at neighboring Al$_1$ sites could be responsible for such an enhancement of the intensity of the band at 23500cm^{-1}. If a clustering mechanism of this type is operating, the predicted third absorption band due to Mn^{3+} in the Al$_1$ position has to be located at higher energies than 26300cm^{-1} or very closely overlap one of the other two intense absorption bands in the observed spectra. In these as well as in spectra of synthetic Mn-andalusite presented by Langer et al. (1976) the absorption band at 14250cm^{-1} invariably exhibits a larger full-width-at-half-maximum value than the

22000cm^{-1} band. This broadness can be attributed either to a large difference between the vibrational constant for the ground state and this particular excited state or to a close overlap beween two absorption bands.

However, lacking substantial evidence for major clustering mechanisms operating in Mn^{3+}-substituted andalusites and also lacking proper evidence for a two-band system appearing under the 14250cm^{-1} band it has been assumed that the band at 23500cm^{-1} is more reasonably assigned to a spin-allowed transition in Mn^{3+} in the Al$_1$ position than to a spin-forbidden transition in Fe^{3+}. The proposed assignments of the major bands in the present spectra are: $^5B_{1g}{\rightarrow}^5A_{1g}$ 14250cm^{-1}, $^5B_{1g}{\rightarrow}^5B_{2g}$ 22000cm^{-1} and $^5B_{1g}{\rightarrow}^5E_g$ 23500cm^{-1}. On the basis of these assignments an energy-level diagram of the split ^5D states of Mn^{3+} in the Al$_1$ position in andalusite can be constructed (Fig. 6) and the CFSE (crystal-field stabilization energy) for Mn^{3+} in that coordina-
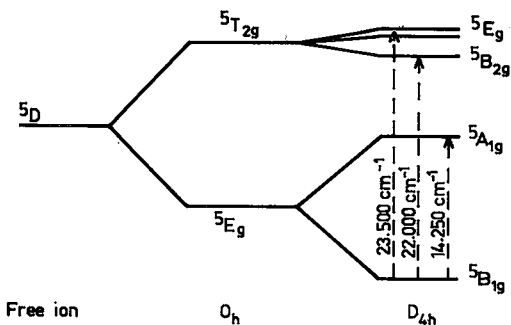
FIG. 6. Energy-level diagram for Mn^{3+} in the Al_1 position in Mn-andalusite, showing the observed transitions.

tion site can be calculated, assuming a D_{4h} symmetry. In this case it has been found to be 47.6 kcal. This value compares with CFSE values for Mn^{3+} in piemontite of 39.9–41.0 kcal. (Burns & Strens 1967), in phlogopite of 46.5 kcal (Burns 1970) and in muscovite of ~43 kcal. (Annersten & Hålenius 1976). In all these examples, Mn^{3+} is octahedrally bonded.

The weaker absorption bands in the spectra at 19450 and 18000cm⁻¹ have also been observed in the spectra of synthetic Mn^{3+}–andalusite (Langer et al. 1976; Langer, pers. comm.); these bands have been assigned to spin-forbidden d–d transitions in Mn^{3+} in the Al_1 position between states derived from ^5D and ^3H states (K. Langer, pers. comm.) The weak band at 11200cm⁻¹ might be assigned to a spin-forbidden transition between states derived from the ^5D and ^1I states.

CONCLUSIONS

The color and pleochroism of Mn-andalusite are caused by the presence of Mn^{3+} in the octahedral Al_1 sites. Both trivalent manganese and ferric iron are strongly ordered into that position. The increasing tetragonal distortion of the Al_1 sites with increasing amount of Mn^{3+} substituting for Al^{3+} is clearly reflected by the shift of the 14250cm⁻¹ absorption band and by the increase of the quadrupole splitting of the Fe^{3+}_{VI} Mössbauer doublet. The CFSE for Mn^{3+} has been found to be 47.6 kcal. The calculation was based on a spectral assignment that assumes the three intense absorption bands at 14250, 22000 and 23500cm⁻¹ to be caused by transitions between the split ^5D states in Mn^{3+} in the Al_1 position.

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