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Infrared Spectra of Al-Fe(III)-Epidotes and Zoisites, $Ca_2(Al_{1-p}Fe^{3+}{}_p)Al_2O(OH)[Si_2O_7][SiO_4]$

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Abstract

Absorption spectra were measured in the range 5000 to 250 cm^{-1} for 26 analyzed zoisites and epidotes, $Ca_2(Al_{1-p}Fe^{3+}{}_p)Al_2O(OH)[Si_2O_7][SiO_4]$, wherein $0.00 < p < 0.11$ (zoisites) and $0.00 < p < 0.89$ (epidotes). From their IR-spectra, both polymorphs can be distinguished by the position of the main OH-valence vibration (zo.: 3260 cm^{-1}; cl-zo. ($p = 0.00$) — ep. ($p = 0.89$): 3326-3365 cm^{-1}), by a band at 2160 cm^{-1}, present only in zoisite, and by completely different band shapes in the ranges 820-700 cm^{-1} and 540-320 cm^{-1}. Appreciable shifts of 5 bands were found to be a function of p, the Fe(III) content of the epidote within the epidote series. These shifts can be represented by the linear equation $\tilde{\nu} = A + Bp$. The values for A (representing the position of each band at $p = 0.00$) and B are as follows: 3325.8 cm^{-1}, +48.3; 1045.6 cm^{-1}, −12.4; 741.7 cm^{-1}, −25.7; 419.4 cm^{-1}, −27.2; 364.2 cm^{-1}, −13.2.

Oxygen-oxygen distances within the O(10)-H···O(4) bridge in the structures of zoisite and epidotes were calculated from the position of the main OH-valence vibration using a Lennard-Jones (6-12) potential function (Bellamy and Owen, 1969) zo.: $R_{IR} = 2.87$ Å; ep.: 2.92 Å ($p = 0.00$) — 2.96 Å ($p = 1.00$). From the presence of a band at 2160 cm^{-1} in all zoisites—which at present can only be interpreted as a low energy OH-valence vibration—we tentatively conclude that some of the protons in zoisite are located in a strong bridge $O(x)\text{-}H\cdots O(y)$ with $R_{IR} = 2.56$ Å. However, it is uncertain which oxygen atoms of the zoisite structure (Dollase, 1968) are involved in this bridge.

Introduction

In recent years, vibrational spectroscopy (*e.g.*, infrared absorption spectroscopy) has been used as a powerful tool for mineral identification ("fingerprint method"), for determination of binary or ternary mixed-crystal compositions (*e.g.*, Mg-Fe-Mn olivines as studied by Burns and Huggins, 1972), and for solving crystal-chemical problems such as clarifying the role of water, hydrogen-bonding effects, and location of protons in mineral structures.

So far, infrared absorption spectra between 4000 and 400 cm^{-1} of one zoisite and one epidote of unknown chemical composition have been published (Moenke, 1962). These spectra differ mainly in the low energy part (<500 cm^{-1}), thus providing the possibility of distinguishing between orthorhombic and monoclinic polymorphs of $Ca_2(Al_{1-p}Fe^{3+}{}_p)Al_2O(OH)[Si_2O_7][SiO_4]$, zoisites, and epidotes.

Furthermore, Strens (1964) measured absorption spectra between 4000 and 650 cm^{-1} of eight epidotes with p between 0.35 and 0.85[1] and concluded that the spectra obtained are identical in all but the finest detail: ". . . those (bands) in the range 1102-884 cm^{-1} appear to show a slight shift with iron content. The magnitude of this shift could not be determined at the resolution of 1 μ = 2 cm employed."

Among the special problems of zoisite and epidote crystal chemistry, the location of protons in both structure types has been worked out by means of single crystal infrared methods (Linke, 1970; Hanisch and Zemann, 1966).

The infrared studies on zoisites and epidotes just outlined left open questions as to (1) the appearance and position of bands below 400 cm^{-1} and their use in the "fingerprint method"; (2) the detection and determination of band shifts with Fe^{3+} content

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[1] A value of 1 wt percent Fe_2O_3 corresponds to $p = 0.06$ Fe^{3+}-ions per formula unit.

(p) in an IR spectral range as wide as possible with modern photometers providing high resolution power; (3) the potential use of these shifts for determination of p in zoisites and epidotes of unknown composition; (4) information about hydrogen bond properties in both mineral structures obtainable from OH vibrations and comparison with X-ray results; (5) rigorous assignment of absorption bands to lattice vibrational modes. The present study deals with some new results obtained in problems 1, 2, 3, and 4.

The formula, $Ca_2(Al_{1-p}Fe^{3+}_p)Al_2O(OH)[Si_2O_7][SiO_4]$, used throughout the present paper is based on recent results of X-ray structure refinements, and Mössbauer and EPR spectroscopy (Dollase, 1968, 1971, 1973; Gabe, Portheine, and Whitlow, 1973; Ghose and Tsang, 1971). These show that in zoisite the two $M_{1,2}$ octahedra[2] per formula are occupied by Al, and that Fe^{3+} substitutes for Al in the M_3 octahedron only. In clinozoisites and epidotes with Fe^{3+} contents up to 0.8 Fe^{3+} per formula, the M_1 and M_2 octahedra are also nearly free from Fe^{3+}, while in epidotes with 0.8–1.0 Fe^{3+} ions per formula unit only up to 12 percent of the total Fe^{3+} content substitutes for Al in the M_1 octahedron. Thus, the above formula is an appropriate approximation for both zoisites and Al-Fe(III) epidotes.

Samples Studied and Experimental Methods

Natural and synthetic zoisites and epidotes covering the compositional ranges p = 0.00–0.11, and p = 0.00–0.89 respectively, studied in the present paper, are listed in Table 1 together with their analyzed Fe^{3+} contents, p, and the literature references, with respect to localities, geology, mineralogy, and chemistry of the samples. References d and e include lattice constants and optical properties of the samples studied. Specimens not described in the literature so far and designated with f were collected at the following localities: KN3, KN4: Unterşulzbachtal, Salzburg, Austria; D44, D45: Dorfer Tal, Osttirol, Austria. The epidotes studied showed no or only weak compositional zoning. On the basis of X-ray analyses, all samples studied were single phases.

Infrared absorption spectra of finely powdered specimens embedded in KBr pellets have been recorded by means of a Perkin-Elmer 325 spectrophotometer covering the spectral range 5000-200 cm^{-1}.[3] The operation conditions are given in Table 2. A spectral slit width of ≤ 2 cm^{-1} was chosen. Thus, absorption bands with a half band width of ≥ 20 cm^{-1} are not broadened by slit errors (Ramsey, 1952).

Experimental Results

Selected infrared spectra, typical for zoisites and epidotes of different Fe^{3+} content, are presented in Figures 1 and 2, respectively. Positions of absorption bands, appearing as single sharp bands, band maxima, or inflections and shoulders in the wings of band systems are compiled in Table 3 for zoisites and in Table 4 for clinozoisites and epidotes. The accuracy is ± 2 cm^{-1} in the range 3600-2000 cm^{-1}, mainly due to the relatively large half band width of bands in this region, and ± 1 cm^{-1} below 1000 cm^{-1} for the case of clearly discrnible bands, maxima, and inflections. The position of bands appearing as shoulders can only be estimated.

It is impossible and in any case unnecessary to reproduce all spectra measured because their shapes develop continuously when proceeding from low to high p-values. This justifies a continuous numeration of equivalent bands in spectra obtained from the various members differing in p within the two series of zoisites and epidotes.

Figures 1 and 2 and Tables 3 and 4 show close similarities of the spectra of both structure types within the regions 1300-820 cm^{-1} and 320-250 cm^{-1}. On the other hand, independent from their compositional parameter p, both structure types differ mainly in the following features: (1) The position of the main OH-stretching vibration at about 3300 cm^{-1} is different (band 2 in zoisite being at 3260 cm^{-1} and band 1 in epidote being at about 3345 cm^{-1}). (2) At about 2160 cm^{-1}, a weak band is present in all zoisite spectra (4) but not in epidote spectra. (3) The strong band 6 of zoisites is clearly split into two main bands 2 and 3 in the epidote spectra. (4) Band 5 of epidotes is either absent or present as much weaker band 7 in zoisites. (5) In the range 820-700 cm^{-1}, only a weak band (13) is present in epidote spectra, while zoisite spectra show three sharp bands of medium intensity, namely 16, 17, and 18. (6) In the range 540-320 cm^{-1}, the spectra of the two polymorphs are completely different.

The zoisite spectra clearly show satellites (bands 1 and 3) of the main ν_{OH}-band (2), probably due to coupling with a lattice vibration at about 100 cm^{-1}. Analog satellites, if present in the case of epidotes, are obscured in the ($\nu_{OH} + \nu_{lattice}$)-range

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[2] Notation according to Dollase (1968).

[3] Pure KBr pellets were used in the reference beam.

by the broad band originating from traces of molecular water in the KBr pellets (*cf* Fig. 2, epidote and KBr-blank spectra).

The very weak but sharp band at 3635 cm^{-1} found in the spectra of both synthetic clinozoisites may be due to the OH vibrations of margarite impurity, though this phase was not detected in the X-ray powder diagram of the synthetic material (K.R. Frentrup, unpublished). Among the hydrous phases of the system $CaO-Al_2O_3-SiO_2-H_2O$ only synthetic margarite shows an OH vibration at this position (Chatterjee, Langer, and Abraham, 1974).

Traces of a calcite contaminant were detected in samples ZOJ, PF 36zo, D45, WI51, and S7 (Table 1) by the presence of a very weak and broad band centered at about 1420 cm^{-1} and attributed to the very intensive ν_3 absorption of the CO_3^{2-} group. The spectrum of sample 7 showed very weak additional bands at 762 and 745 cm^{-1}, most probably due to a trace of albite.

All spectra showed a broad, weak band at 1630 cm^{-1}, the deformation vibration of molecular water traces.

From Table 4 it is evident that some epidote bands show systematic shifts with increasing Fe^{3+} content p. Among these, bands 1, 5, 13, 26, and 28 are measurable with good accuracy (see above), because they appear as single sharp bands or maxima. Shifts of bands 3, 5, and 9 were already found in principle, though not measured, by Sterns (1964).

The positions of bands 1, 5, 13, 26, and 28 are plotted against the Fe^{3+} content of the epidote samples in Figures 3 and 4, assuming an analytical error of $+ 0.01$ p.[4] The data could easily be fitted by linear regression equations

$$\bar{\nu} = A + Bp \qquad (1)$$

Their coefficients, A and B, are given in Table 5. A represents the position of each band in case of the iron(III)-free composition ($p = 0.00$), and B the slope of the lines. The equations are represented in Figures 3 and 4 by dashed lines.

In the spectra of zoisites studied so far, shifts comparable in magnitude to those of epidote bands were not found (Table 1). However, this may well be due to the small compositional range $0.00 < p < 0.11$ of zoisites available in the present study. It should finally be pointed out that both synthetic samples PF39cz and PF41cz, identified from their powder X-ray patterns as the monoclinic polymorph of $Ca_2Al_2AlO(OH)[Si_2O_7][SiO_4]$, independently proved to be clinozoisites on the basis of their infrared spectral properties. This is evident from the shape of their spectra (Fig. 2), and from the positions of their bands 1, 5, 13, 26, and 28 as well (Figs. 3, 4).

TABLE 1. Zoisites and Epidotes, $Ca_2(Al_{1-p}Fe^{3+}_p)Al_2O(OH)[Si_2O_7][SiO_4]$, Studied

Sample No.	Source*	Fe_2O_3 wt %	p	Sample No.	Source*	Fe_2O_3 wt %	p
			Ortho-Zoisites				
PF36zo	a	0.0	0.00	S439	c	1.19	0.07
ZOJ	b	0.0	0.00	Zo 3b	d	1.68	0.10
S240	c	0.20	0.01	S1644	c	1.75	0.11
			Clino-Zoisites and Epidotes				
PF39cz	a	0.0	0.00	HU12	e	8.21	0.49
PF41cz	a	0.0	0.00	HU261	e	9.03	0.53
RA173	e	3.80	0.23	D45	f	10.2	0.61
HU252	e	5.00	0.29	Wi51	e	11.48	0.68
HU74	e	5.27	0.31	D44	f	11.9	0.71
HU205	e	6.22	0.37	KN4	f	12.0	0.72
HU266	e	6.52	0.38	KN3	f	12.0	0.72
HU34	e	6.64	0.39	KN1	e	14.25	0.86
HU283	e	6.68	0.40	S7	e	14.40	0.87
HU215	e	7.51	0.44	EPT	e	14.71	0.89

**a and b, synthetic material kindly made available (along with unpublished results) by K.R. Frentrup, Inst. Mineral. Ruhr-Univ. Bochum (a), and by Professor Dr. W. Johannes, Inst. Mineral. Tech. Univ. Hannover (b); c natural (Schmidt, 1972); d natural (Mottana et al, 1968); e natural (Hörmann and Raith, 1971); f natural, Fe_2O_3 contents determined during the present study.*

Discussion

The above results show that the structure type of epidote-group minerals, ortho- and clinozoisites or epidotes, can be readily and conclusively identified by certain properties of their infrared spectra. Features 1, 2 and 6 mentioned in the preceding section can be best used for this purpose, feature 1 being valuable, if only NaCl- or KBr-prism instruments are available. A special advantage

TABLE 2. Run Conditions of IR Absorption Spectra of Al-Fe(III)-Epidotes and Zoisites

Spectral range [cm^{-1}]	3700-2900 2300-2000	1300-1000	1000-450	450-250
Sample concentration	1.5 ± 0.2 mg / 450 ± 10 mg KBr			
KBr-Pellet Dimensions	diameter 13 mm; thickness 1.28 ± 0.05 mm			
Spectral Slit Width	$\leqslant$ 2 cm^{-1}			
Scan Speed [cm^{-1}/min]	24	13	5	2.8
Abscissa [cm^{-1}/cm]	50	25	30	30
Ordinate Expansion	3.0	1.3	1.3	1.3

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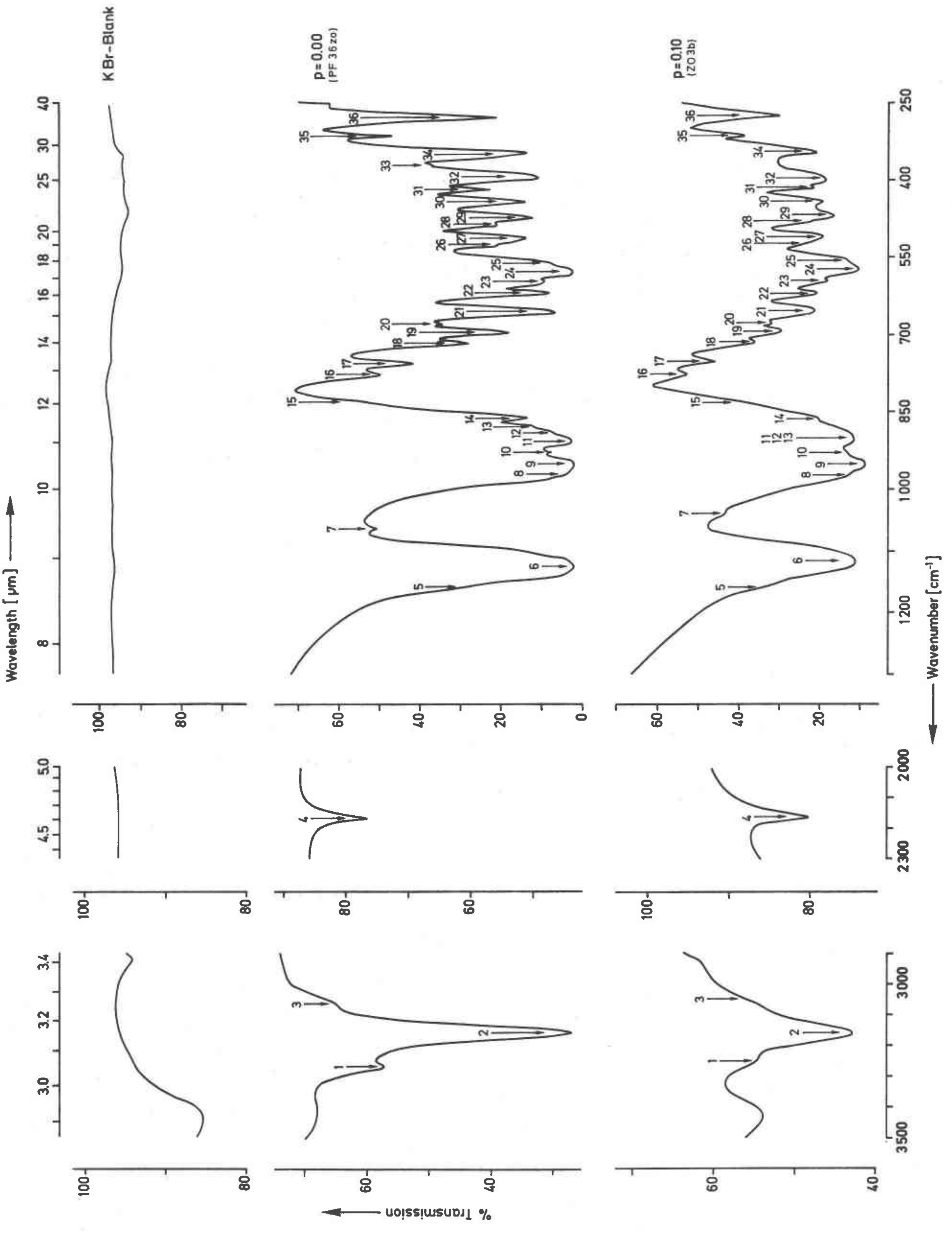
[4] *i.e.*, an uncertainty of about ±0.1 wt percent Fe_2O_3. The accuracy of position measurements was given above.



K Br-Blank
p = 0.00 (PF 36 zo)
p = 0.10 (ZO3b)
Wavelength [μm]
Wavenumber [cm⁻¹]
% Transmission
3.0
3.2
3.4
4.5
5.0
8
10
12
14
16
18
20
25
30
40
3500
3000
2300
2000
1200
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of infrared spectroscopy is that rapid measurements can be made with samples as small as about 1 mg (Table 1) or even 10 μg, if micro-sampling techniques are used. Thus, only a few crystals need to be separated from a rock. It is obvious that this is also true for the determination of p, the Fe^{3+} content in the formula unit of Al-Fe(III) epidotes of unknown composition, which can be readily done by measuring the position of bands 1, 5, 13, 26, and 28 and solving equation (1) for p with the requisite parameters given in Table 5. With operational conditions comparable to those specified in Table 2, the determination of p is accurate to about ± 0.04 with bands 1, 13, and 26, and to about ± 0.08 with bands 5 and 28. Using the ordinate and abscissa expansions given below Table 5, p can be determined to ± 0.01 from band 13. These accuracies are in the same order of magnitude as for determinations based on optical or X-ray methods (Hörmann, and Raith, 1971). Using n_β or the birefringence, $(n_\gamma - n_\alpha)$, Fe^{3+} contents can be obtained with an accuracy of about $\pm 0.03\ p$, using $2V_\alpha$ with about $\pm 0.04\ p$ (100-80°) and about ± 0.06 (80-70°). With the most suitable X-ray property, $\Delta\ 2\theta$ (020Ep-111Si) (Cu$K\alpha$), p is accurate within about ± 0.03. As in case of chemical or X-ray determinations of the Fe^{3+} contents, mean values are obtained by the IR methods suggested.

As stated in the introduction, no attempt is made here to solve the problem of a rigorous band assignment for the complicated vibrational absorption spectra of zoisite and epidote. However, it should be mentioned that on the basis of Lazarev's (1961) interpretation of zoisite and epidote IR-reflection spectra (Matossi and Krüger, 1936), bands 6, 7, 9, 11, 14, and 19 + 20 of zoisites and bands 2, 3, 5, 7, 9, 11, and 16 of epidotes in the spectra of the present study can be assigned to Si-O valence vibrations of SiO_4 and Si_2O_7 groups. Band 10 of zoisite and 8 of epidotes are probably due to an OH-librational mode, which was found in some layer silicates at about 930 cm^{-1} (Stubican and Roy, 1961; Vedder and McDonald, 1963; Russell, Farmer, and Velde, 1970). This suggestion requires confirmation by measurements using synthetic OD forms of zoisite and clinozoisite.

The spectra of both structure types are completely different in the whole low energy range (540 cm^{-1}) except band 36 of zoisite and 34 of clinozoisites and epidotes (Tables 3 and 4, Figs. 1 and 2). From this, it may be assumed that the bands in question are due to a Ca-O vibration. In addition, the behavior of the bands in question corresponds quite well qualitatively with mean Ca-O distances: the energy of band 36 in zoisite is somewhat higher than that of 34 in clinozoisite in conformity with the shorter Ca-O average in zoisite (Dollase, 1968), while the shift of band 34 in epidotes towards lower energies with increasing p corresponds to the increase in the mean Ca-O distance with p in this structure type (Gabe *et al*, 1973).

From the completely different spectral shapes of both structure types in the ranges 820-700 cm^{-1} and 540-320 cm^{-1}, it seems to be evident that bands in these regions originate mainly from M-O vibrations within the different octahedra chains.

For a discussion of the behavior of OH-valence vibrations in epidotes and zoisite, it should be remembered that on the basis of (1) crystal chemical arguments already given by Ito, Morimoto, and Sadanaga (1954), (2) bond strength calculations for oxygen atoms (Dollase, 1968; Gabe *et al*, 1973), and (3) IR experiments with oriented crystal sections using polarized radiation (Hanisch and Zemann, 1966; Linke, 1970), it was concluded that hydrogen atoms are bonded in both structure types to O(10) so as to form a hydrogen bridge to O(4); see Figures 2 and 3 of Dollase (1968). As derived from the refined structures of clinozoisite and zoisite, the oxygen distances in the bridge $\underbrace{\mathrm{O(10)\text{-}H\cdots O(4)}}$, symbolized R_X, are 2.89 Å and 2.76 Å respectively (Dollase, 1968), indicating stronger hydrogen bonding in zoisite. Gabe *et al* (1973) showed that R_X increases with increasing Fe^{3+} content p in epidotes. Distances (symbol, R) in hydrogen bridges X-H··Y can be independently calculated from the energy of the X-H valence vibration, *eg.*, by using a Lennard-Jones (6-12) potential function, as shown by Bellamy and Owen (1969) who gave the equation

$$\Delta\nu_S = 50\left[\left(\frac{d}{R}\right)^{12} - \left(\frac{d}{R}\right)^{6}\right] \qquad (2)$$

$\Delta\nu_S$ is the frequency difference in cm^{-1} between the vibration of the free X-H group and the position of the X-H vibrational band of the hydrogen-bonded group; in case of $X = Y =$ oxygen, then $\Delta\nu_S = 3700 - \nu_{OH}$, while d is approximately the sum of the colli-

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FIG. 1. Two typical infrared absorption spectra of orthozoisites of Table 1 with different Fe^{3+} contents, p. Spectral regions without absorption bands are omitted. Band numbers refer to those in Table 3.

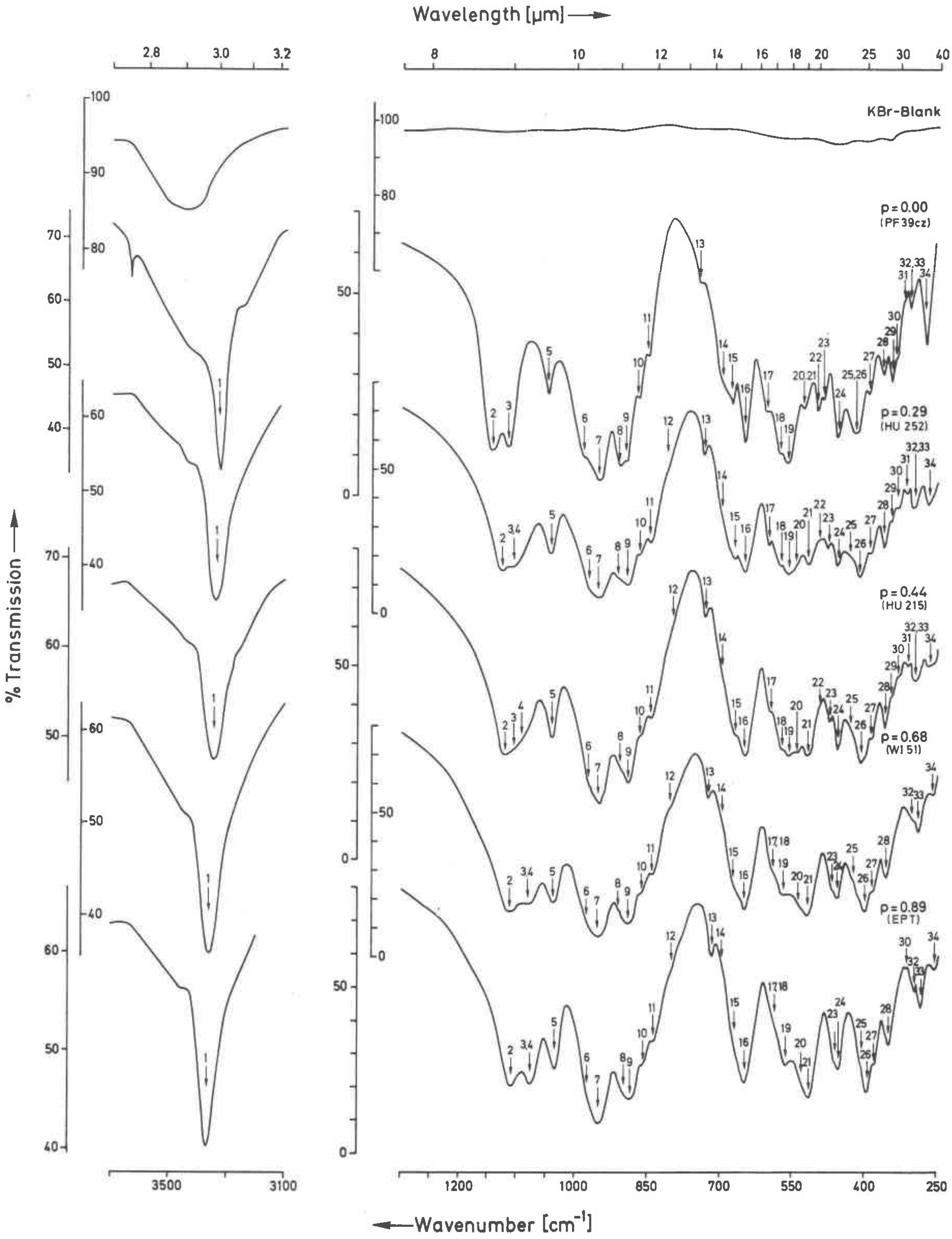

FIG. 2. Some typical infrared absorption spectra of clino-zoisites and epidotes of Table 1 with different Fe^{3+} contents, *p*. Spectral regions without absorption bands are omitted. Band numbers refer to those in Table 4.

TABLE 3. Fe^{3+}-Contents, *p*, and Position of Bands (in [cm^{-1}]) in the IR Absorption Spectra of Some Zoisites of Table 1

Sample No. p Band No.	PF 36 zo 0.00	S 240 0.01	Zo 3b 0.10	Sample No. p Band No.	PF 36 zo 0.00	S 240 0.00	Zo 3b 0.10
1	3270	3260	3255	19	695	697	693
2	3160	3153	3157 sh	20	679	679	677
3	3065 sh	3050 wsh	3060 wsh	21	655	655	654
4	2165	2161	2160	22	618	619	619
5	1158 wsh	1160 wsh	1158 wsh	23	593	595	595
6	1125	1116	1116	24	578	572	572
7	1064	1043	1040 wsh	25	562 sh	557 wsh	556 wsh
8	970 sh	975 wsh	973 sh	26	524 sh	523 wsh	522 wsh
9	950	949	950	27	512	511	511
10	928	929	928 wsh	28	486	485 wsh	481 wsh
11	906	907	901	29	472	469	470
12	890 wsh			30	442	444	444
13	878	880 wsh		31	418	415	415
14	860	863	863	32	394	398	398
15	830 wsh	834 wsh	832 wsh	33	370		
16	777	778	774	34	349	342	343
17	755	756	752	35	314	312	312
18	717	715	714	36	279	278	278

sh = shoulder, wsh = weak shoulder

TABLE 4. Fe^{3+}-Contents, *p*, and Position of Bands (in [cm^{-1}]) in the IR Absorption Spectra of Some Clino-Zoisites and Epidotes of Table 1

Sample No. p Band No.	PF 39 cz 0.00	HU 252 0.29	HU 215 0.44	WI 51 0.68	EP T 0.89
1	3326	3338	3345	3360	3365
2	1143	1126	1120	1110	1108
3	1116	1106	1100 wsh	1079	1076
4			1090 wsh		
5	1047	1043	1039	1037	1035
6	980 sh	973 wsh	977 wsh	980 wsh	975 wsh
7	950	954	952	953	951
8	906	910 wsh	905 wsh	910 wsh	900 wsh
9	895	892	889	889	886
10	869	865 sh	865 sh	862 sh	861
11	849	843	843	840	836
12		805	800 wsh	802 wsh	800 wsh
13	741	733	731	723	718
14	690 sh	695 wsh	697 wsh	697 wsh	697 wsh
15	676	670	668 sh	673 wsh	670 wsh
16	650	649	648	649	648
17	603	599	596 sh	590 wsh	585 wsh
18	575	575	571		
19	561	558	557	568	563
20	527	544 wsh	541	530 wsh	
21		517	518	519	517
22	498	495 wsh	495 wsh		
23	487	477	474	467	460 wsh
24	457	457	457	457	454
25		430 wsh	430 wsh	430 wsh	410 wsh
26	419	411	408	400	395
27	393	389	387	385 sh	381
28	363	360	359	355	351
29	344	345 sh	346 wsh		
30	336 sh	338	331 sh		
31	320 wsh	314	312		313
32	305	299	295	300	297
33				289	284
34	274	268	265	260	256

sh = shoulder, wsh = weak shoulder

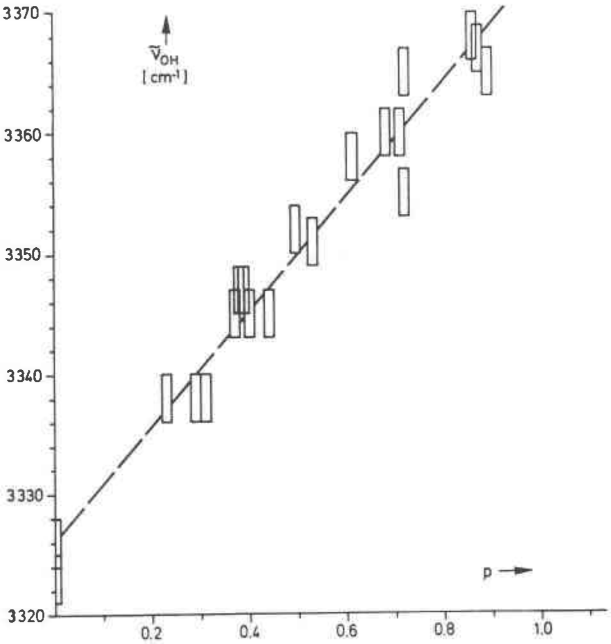

FIG. 3. Position of OH-valence vibration (band 1) of all clino-zoisites and epidotes studied (*cf* Table 1) as a function of Fe^{3+} content, *p*. The dashed line represents the linear regression equation (1), the coefficients of which are given in Table 5.

sion radii of *X*- and *Y*-atoms involved in the bridge. Actually, if $X = Y =$ oxygen, $d = 3.35$ Å (Bellamy and Owen, 1969). Thus, from our IR data, namely the OH-band position in clinozoisite (band 1, Table 4) and the shift of the band with increasing Fe^{3+}-content *p* (Fig. 3, Table 5), we calculated oxygen distances, R_{IR}, in the bridge O(10)-H···O(4) for the whole Al-Fe(III)-epidote series, $0.00 < p < 1.00$. The result is given as the solid line in Figure 5. Figure 5 also shows distances, R_X, as derived from X-ray structure refinements done so far. It can be seen that R_{IR} is about 1.3 percent higher than R_X for $p = 0.00$, while R_{IR} and R_X seem to converge with increasing *p*. The small discrepancy may be due to a slight declination of the hydrogen bridge from linearity, a presupposition made when using the Lennard-Jones (6–12) potential function. A slightly bent hydrogen bridge in epidote is also indicated by the results of Hanisch and Zemann (1966; *cf* Fig. 3). From the "normal" OH band in zoisite (no. 2, Table 3) we calculate an O(10)-H···O(4) distance $R_{IR} = 2.87$ Å, again somewhat higher than the X-ray distance $R_X = 2.76$ Å (Dollase, 1968), the difference probably indicating a slightly higher bending angle of the bridge as compared with epidote.

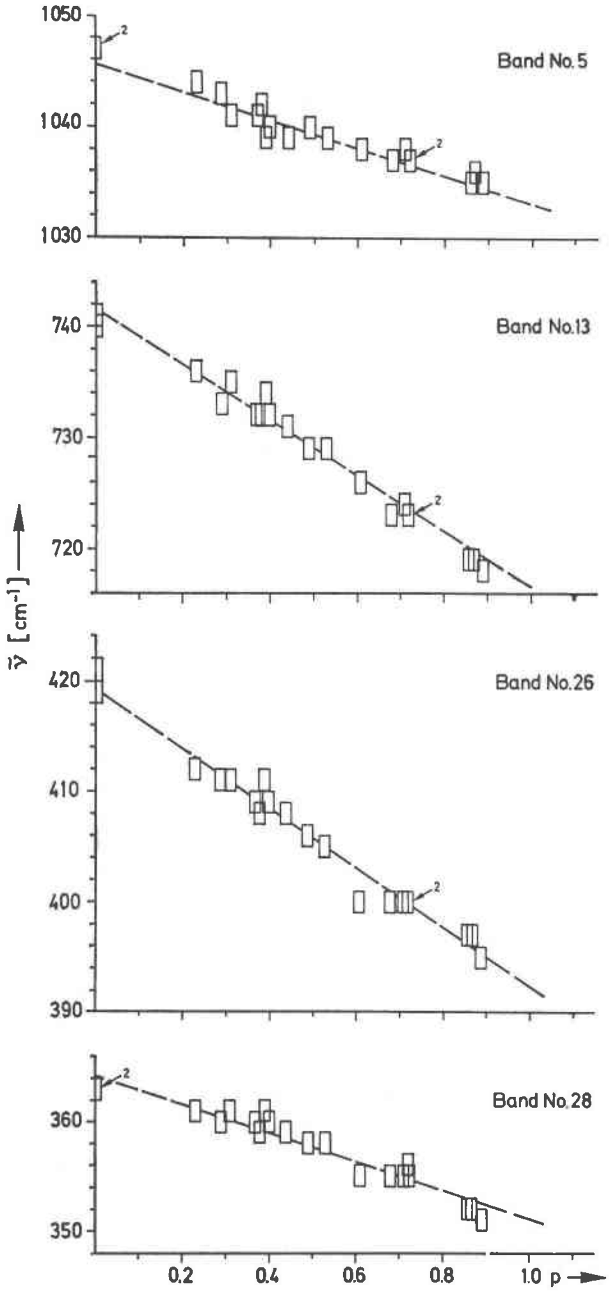

FIG. 4. Position of some lattice vibrations of all clino-zoisites and epidotes studied (*cf* Table 1) as a function of Fe^{3+} content, *p*. Only bands 5, 13, 26, and 28 (see Fig. 2), which appear as single bands and show significant shifts, have been used. The meaning of the dashed lines is as in Figure 3. The numeral 2 indicates two samples with the same *p* and $\tilde{\nu}$ value.

TABLE 5. Coefficients *A* and *B* for Linear Regression Equation $\tilde{\nu} = A + Bp$ [cm^{-1}], Relating Position of Some Bands in the IR Absorption Spectra to Fe^{3+}-Contents, *p*, of Epidotes

Band No.	A	B
1 (ν_{OH})	3325.8 ± 1.3	+48.3 ± 2.3
5	1045.6 ± 0.9	-12.4 ± 1.6
13	741.7 ± 0.5 741.4 ± 0.3*	-25.7 ± 0.8 -25.3 ± 0.5*
26	419.4 ± 0.5	-27.2 ± 1.0
28	364.2 ± 0.5	-13.2 ± 0.8

Expansion: abscissa 10 cm^{-1}/cm, ordinate x 3.5.

Besides bands 1–3 (Table 3) between 3330 and 3000 cm^{-1}, all zoisites show an additional band in the high-energy range of their spectra, namely band 4 at 2160 cm^{-1}. This band cannot be attributed to possible trace contaminations, especially not to CO_3^{2-} vibrations of calcite traces. This is because CO_3^{2-} has its highest energy vibration, ν_3, at 1429–1492 cm^{-1} (Nakamoto, 1963). There are no possible trace impurities showing bands near 2160 cm^{-1}, except CO_2 molecules with ν_3 at 2349 cm^{-1} (gaseous state, Nakamoto, 1963). However, the position of CO_2-ν_3 does not fit with that of the band in question and, in addition, it seems very unlikely that CO_2 molecules could be trapped in the zoisite structure because of their size. The band in question can also not

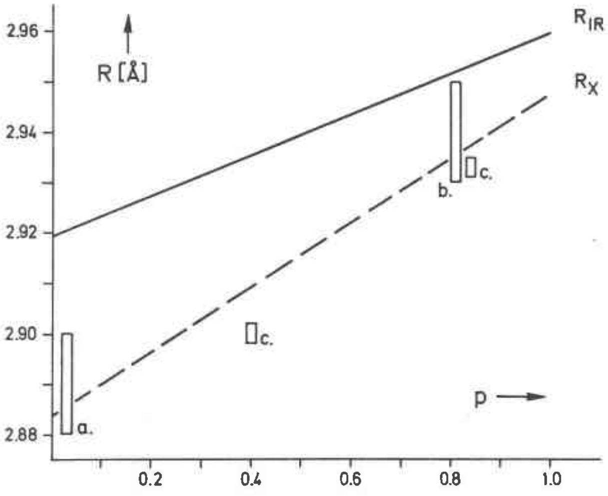

FIG. 5. Oxygen distance, *R*[Å], within the hydrogen bridge $\underbrace{O(10)\text{-}H\cdots O}(4)$ in the structure of clino-zoisites and epidotes as a function of Fe^{3+} content, *p*. R_X: calculated from X-ray structure refinements (**a.** Dollase, 1968; **b.** Dollase, 1971; **c.** Gabe *et al*, 1973). R_{IR}: calculated from OH-valence vibration (see Fig. 3 and Table 5) on the basis of a Lennard-Jones potential (Bellamy and Owen, 1969).

be due to a combination vibration of the 3160 cm^{-1} OH valence vibration with a lattice vibration at about 1000 cm^{-1}, ($\nu_{\text{OH}} - \nu_{\text{lattice}}$), because measurements between 5000 and 4000 cm^{-1} did not reveal the corresponding ($\nu_{\text{OH}} + \nu_{\text{lattice}}$)-band expected at about 4160 cm^{-1}. Furthermore, overtones of low energy vibrations to be expected in the 2000-2300 cm^{-1} region; *e.g.*, that first overtone of the Si-O-vibration at 1115 cm^{-1} cannot be observed at the low sample concentrations used in the KBr-pellet technique.[5] Thus, a possible explanation of the 2160 cm^{-1} band of zoisites seems to be a low energy OH-vibration. If this interpretation is correct—and there is no reason for us at present to doubt this—it may be tentatively concluded that a part of the protons present in the zoisite structure is not bound to O(10) but to another oxygen atom, O(x). If so, O(x) should show a short distance to its next oxygen neighbor, O(y), thus giving a strong bridge, $\underbrace{\text{O}(x)\text{-H}\cdots\text{O}}(y)$. From the position of band 4 we obtain a distance $R_{\text{IR}} = 2.56$ Å by use of Eq. (2). O(x) can only be an oxygen atom with a bond strength below 2.00. This is true for O(4), O(7), and O(8) in zoisite, their bond strengths from Dollase (1968) being 1.50, 1.57, and 1.50, respectively. O(4) can presumably not be the O(x) atom in the short hydrogen bridge under discussion, because it is the acceptor in the "normal" bridge $\underbrace{\text{O}(10)\text{-H}\cdots\text{O}}(4)$. Thus, O(7) and O(8) remain possible as O(x) in the short bridge. We tried to identify atom O(y) by a calculation of all O(8) and O(7) oxygen distances in the zoisite structure in order to check whether a distance O(8)-O(y) or O(7)-O(y), comparable to R_{IR}, does indeed exist in the structure. However, such short distances were only found between oxygen atoms forming edges of the coordination polyhedra. For examples O(8) [$x = 0.9954$, $y = 0.7500$, $z = 0.2950$] is separated by 2.636 Å from O(3) [$x = 0.1012$, $y = 0.4850$ or 0.0150, $z = 0.4300$], all three oxygen atoms belonging to the Al(3)-oxygen octahedron. A relatively short distance, $R_X = 2.740$ Å, exists between O(7) [$x = 0.4905$, $y = 0.2500$, $z = 0.3360$] and O(3) [$x = 0.3584$, $y = 0.9900$, $z = 0.2452$], belonging to different coordination polyhedra. However, the X-ray distance, R_X, is significantly higher than R_{IR}. At present, therefore it is uncertain which oxygen atoms are involved in the short bridge $\underbrace{\text{O}(x)\text{-H}\cdots\text{O}}(y)$ inferred from the infrared spectra of zoisites. Measurements of the pleochroic scheme of band 4 in zoisite single crystals with polarized radiation may help to solve this problem.

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[5] The first overtone of the OH-bending is normally also not observed in KBr spectra and, if present, should be expected at lower energies (*ca* 1950–2000 cm^{-1}) if we apply the findings of Stubican and Roy (1961), Vedder and McDonald (1963), and Russell *et al* (1970) on the OH-bending fundamental in layer silicates.

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