The crystal chemistry of the humite minerals:
Fe^{2+}-Ti^{4+} charge transfer and structural allocation of Ti^{4+} in chondrodite and clinohumite

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Abstract: Single crystals of the humite-group minerals, with general crystal chemical formula $n \cdot [M_2SiO_4] \cdot [M_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}]$ where M is predominantly Mg eventually substituted by Fe^{2+}, are studied by electron microprobe analysis, X-ray diffraction and polarised electronic absorption spectroscopy, in the present paper two chondrodites (n = 2) and four clinohumites (n = 4). The aim was to elucidate colour and pleochroism of such minerals and to evaluate their local crystal chemical properties, esp. the structural allocation of Ti^{4+}.

The dominating features of all spectra are: (i) a slightly polarised absorption edge in the UV at energies > 35000 cm⁻¹; (ii) a strong and broad band at 23300 cm⁻¹ with band widths near 6000 cm⁻¹ and strongly polarised with $E||X$ in all specimen of the two minerals; and (iii) a complex low energy band system in the NIR (11600 cm⁻¹ in $E||X$, 9500 cm⁻¹ in $E||Z$ and 7700 cm⁻¹ in $E||Y$) which corresponds in all details to the dd-band system in olivines caused by Fe^{2+} in (M1) and (M2). Such spectral properties explain the observed colour and pleochroism, **X** golden yellow to orange, **Y** and **Z** light yellow to almost colourless. The band properties of (ii) are typical of excitation of metal-metal charge transfer, MM-CT, the band energy is consistent with that expected for MM-CT in $Fe^{2+}Ti^{4+}$ pairs at a distance near 3.2 Å. The analysis of the relation between optical and crystallographic vectors in the minerals studied suggests that the FeTi-CT interaction occurs predominantly along the polyhedral units $M2_5M3M3M2_5$ in the structures of both chondrodite and clinohumite as it is the case for the iron-rich clinohumite of Platonov *et al.* (2001). The evaluation of all information obtained suggests that Ti^{4+} is allocated in the M3 positions of the low-titanium chrondrodites and clinohumites studied.

Key-words: chondrodite, clinohumite, Fe-Ti charge transfer, Ti allocation, electronic absorption spectroscopy.

1. Introduction

The humite minerals may be represented by the crystal chemical formula $n \cdot [M_2SiO_4] \cdot [M_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}]$, where n takes integer values from 1 to 4 for orthorhombic norbergite with space group (SG) *Pbnm* and *Z* = 4, monoclinic chondrodite with SG = $P2_1/b$ and *Z* = 2, orthorhombic humite with SG = *Pbnm* and *Z* = 4 and monoclinic clinohumite SG = $P2_1/b$ and *Z* = 2, respectively. M is predominantly Mg and to a smaller extent Fe and also Mn, Ca, Zn.

The crystal structures of the humite minerals were determined by Bragg & West (1927) and Taylor & West (1928) and later refined by Gibbs *et al.* (1970), Ribbe & Gibbs (1971), Robinson *et al.* (1973), Kocman & Rucklidge (1973), Fujino & Takeuchi (1978) and Platonov *et al.* (2001). The space groups quoted above are those of the structure determinations and refinements referred to.

The structures of the humite minerals are made up by a slightly distorted hexagonally dense 2H package of anions

(O^{2-}, F^-, OH^-). In this respect, the humite mineral structures are closely related to the olivine structure which is also based on a nearly ideal 2H package of oxygen. As in the olivine structure type, in the structures of all humite minerals 1/2 of the octahedral voids are occupied by the M cations while the occupancy of the available tetrahedral voids decreases from 1/8 in olivine over 1/9 in clinohumite (n = 4) to 1/12 in norbergite (n = 1). In contrast to olivines where the M1 octahedra are edge-connected to form continuous straight chains parallel to **c** (*Pbnm*-setting) with M2 octahedra alternately attached on either side of the M1 chain, such that M2M1 zig-zag chains are formed, the humite minerals contain, due to another type of ordering of the M cations over the available octahedral sites compared to olivine, fragments of such zig-zag chains of edge-connected octahedra (*cf.* Ribbe 1980). These fragments will be shown and discussed for chondrodite and clinohumite studied in this paper, in the results and discussion section in connection with the interpretation of the results to be presented here.

Except for the coordinating ligands, the geometrical properties, such as mean M-O distances and distortion parameters, of the octahedra forming the chain fragments, resemble closely those of the M1 and M2 octahedra in olivines (*cf.* Fig. 7, Platonov *et al.*, 2001). The coordination in the various types of octahedra is made up in all humite structures, by six oxygen atoms in the case of M1 octahedra, in clinohumite $M1_c$ and $M1_n$ octahedra, and also $M2_6$ octahedra. In contrast, the $M2_5$ and M3 types of octahedra occuring in the humite mineral structures contain (F,OH): $M2_5[(O_5)(F,OH)]$ and $M3[(O_4)(F,OH)_2]$. It is obvious that their number per volume unit increases on decreasing n. OH^- may be replaced in stoichiometric amounts by O^{2-} to provide charge balance for any Ti^{4+} substituting for M^{2+} (*cf.* the above general formula).

With respect to the intracrystalline distribution of the main substitutive cations, all investigators agree that ferrous iron is ordered in approximately equal amounts in the most distorted octahedra M1 and $M2_6$ (70 to 90 % of Fe^{2+}), but is nearly absent in the less distorted octahedra M3. As it was noted by Robinson *et al.* (1973) and Fujino & Takeuchi (1978), in high-ti-

tanium clinohumites $M2_5$ and M3 sites may be also enriched in Fe, in contrast to Ti-poor clinohumites. It is important to note further that all evidence from structure determinations on humite minerals rich enough in titanium to be differentiated from other cations, points to an ordered distribution of Ti^{4+} into the M3 (Jones *et al.*, 1969; Fujino & Takeuchi, 1978; Ribbe, 1979, 1980). Such information is still lacking for the more common Ti-poor humite minerals.

In any case, the structural and chemical features of the humites provide strong reason to expect charge transfer interaction between Fe^{2+} and Ti^{4+}, replacing Mg in adjacent edge-sharing octahedra, which may then explain the distinct golden-yellow to red-orange pleochroism of these minerals: **X > Y > Z** (Larsen, 1928; Tröger, 1971; Deer *et al.*, 1982) or **X > Z > Y** (Winchell & Winchell, 1951). It is the aim of the present paper to obtain from electronic absorption spectroscopy, information on possible metal-metal charge transfer in the humite minerals chondrodite and clinohumite and about the distribution of any substitutive Ti^{4+} in their structures.

Table 1. Sources, electron microprobe analyes, optical orientations and thicknesses of platelets of the humite minerals studied.

Sample	260	15/84	Kl-2	Ku-5	SL-387	PS-92/94
Mineral	Chondrodite	Chondrodite	Clinohumite	Clinohumite	Clinohumite	Clinohumite
Source	Kocherova, Ukrainian shield, Ukraine	Sparta, New Jersey, USA	Kukhilal, SW Pamir, Tadjikistan	Kugda, Eastern Siberia, Russia	Kimberlite pipe Sludyanka, Yakutia, Russia	Kimberlite pipe Bazovaya-3, Yakutia, Russia
SiO_2	35.96	35.45	38.07	37.60	36.96	34.74
TiO_2	0.26	0.19	2.77	1.58	0.71	2.89
FeO	0.78	1.45	0.25	4.77	8.77	13.14
MnO	0.05	0.14	0.02	0.23	0.32	0.26
MgO	57.29	56.54	55.57	52.62	49.39	43.46
CaO	0.06	0.04	0.01	0.01	–	0.01
NiO	0.04	–	0.07	0.10	–	–
ZnO	0.12	–	0.09	016	–	–
Total	94.56	93.80	96.85	97.07	96.18	94.50
Si, pfu	2.069	2.038	3.958	3.985	4.018	3.934
Ti	0.011	0.008	0.217	0.126	0.058	0.246
Fe	0.038	0.070	0.022	0.423	0.796	1.245
Mn	0.002	0.007	0.002	0.020	0.029	0.025
Mg	4.909	4.845	8.613	8.313	7.990	7.368
Ca	0.004	0.002	0.001	0.001	–	0.003
Ni	0.002	–	0.006	0.008	–	–
Zn	0.005	–	0.007	0.013	–	–
Σ_{oct}	4.971	4.932	8.868	8.904	8.873	8.887
	1.⊥AB(**Z**)	1.∥OAP	1.⊥AB(**Z**)	1.∥OAP	1.∥OAP	1.∥OAP
	X, Y	**X, Z**	**X, Y**	**X, Z**	**X, Z**	**X, Z**
	165 μm	415 μm	395 μm	85 μm	28 μm	15 μm
	2. ⊥ OB(**X**)	**2. ⊥ AB(Z)**	**2. ⊥ OB(X)**	**2. ⊥ AB(Z)**	**2. ⊥ AB(Z)**	
	X, Z	**X, Y**	**X, Z**	**X, Y**	**X, Y**	
	168 μm	403 μm	307 μm	142 μm	76 μm	

The atoms per formula units, pfu, were calculated on the basis of 18 or 34 negative charges in the formulae of chondrodite or clinohumite, respectively.

Total iron was calculated as FeO. AB = acute bisectrix; OB = obtuse bisectrix; OAP = plane of optical axes; **X**, **Y** and **Z** (= α, β and γ, respectively, or = N_p, N_m and N_g, respectively) = the three mutually perpendicular, principle vibration axes of the optical indicatrix of biaxial minerals. The last horizontal section presents the optical orientations of the two platelets, 1. and 2., prepared for each mineral sample: The first, second and third lines give the plates' orientations, the vibrational directions parallel to which spectra with linearly polarized light **E**, can be recorded, and the plates' thicknesses, respectively.

2. Samples and methods

The minerals studied, their sources, chemical compositions as well orientations and thicknesses of crystal sections prepared for polarised spectroscopy are compiled in Table 1.

Microprobe analyses of the samples were obtained by a JCXA-777 electron microprobe (Technical Service Center, Academy of Science of Ukraine) on those spots of the plates on which the spectra were measured. The following standards were used in the analyses: synthetic quartz (Si), rutile (Ti), fayalite (Fe), rhodonite (Mn), periclase (Mg), wollastonite (Ca), sphalerite (Zn) and metallic nickel (Ni).

The crystal plates mentioned in Table 1 were polished on both sides. As one can see from slabs´orientations, the spectra could be obtained along all three optical indicatrix axes of all the mineral specimen studies: $\mathbf{E}||\mathbf{X}$, $\mathbf{E}||\mathbf{Y}$ and $\mathbf{E}||\mathbf{Z}$.

For the evaluation of the spectra, we need not only to check and confirm the optical orientations of the mineral plates (Table 1), but do need also to know the relations between the orientations of the main optical vectors $\mathbf{X}$, $\mathbf{Y}$ and $\mathbf{Z}$ to the crystallographic vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ within the plates. Care is necessary here, as different settings of the monoclinic space group no. 14 of the International Tables for X-Ray Crystallography, valid for both structures, are used in the literature (*cf.* Jones, 1969). We refer here always to the first setting of no. 14, $P2_1/b$, which was used in all structure determinations and refinements done so far (*cf.* introduction). The orientation relations with respect to this setting were checked by determining the positions of the crystallographic axes relative to the optical directions in plate no. 2 of chondrodite 15/84 as well as plate no. 2 of clinohumite Ku-5, using X-ray CCD methods of single-crystal structure research.

The polarised single-crystal spectra were scanned at room temperature using the microspectrometer ZEISS UMSP-80 (TU Berlin) in the spectral range 35000–7000 cm^{-1}. Experimental details of such measurements are described elsewhere (Langer, 1988). The energy positions of the band maxima, $\tilde{v}$ [cm^{-1}], the full band widths at half band heights, $\Delta\tilde{v}_{1/2}$ [cm^{-1}], and the band intensities, in terms of linear absorption coefficients, $\alpha = [\log(I_o/I)]/t$ [cm^{-1}] with t = plate thickness, were obtained by peak fitting procedures (Program PeakFit, Jandel Scientific 1991) assuming Gaussian shape of the bands.

3. Results and discussion

The chemical compositions (Table 1) of the minerals studied differ as expected in the magnesium contents in accord with their crystal chemical formulae. In addition, they exhibit different Fe and Ti contents. Iron ranges from 0.022 apfu in clinohumite Kl-2 to 1.245 apfu in clinohumite PS-92/94, and titanium varies from 0.008 apfu in chondrodite 15/84 to 0.246 apfu in clinohumite PS-92/94.

Polarised absorption spectra of chondrodite no. 15/84 and of clinohumite no. Ku-5 are displayed in Fig. 1. Note that the ordinate in the clinohumite spectra is compressed by 1:8.8 compared to that of the chondrodite spectra for better comparison. The spectra of the two humite minerals are typical of all the respective mineral specimen of Table 1. They show the following features:
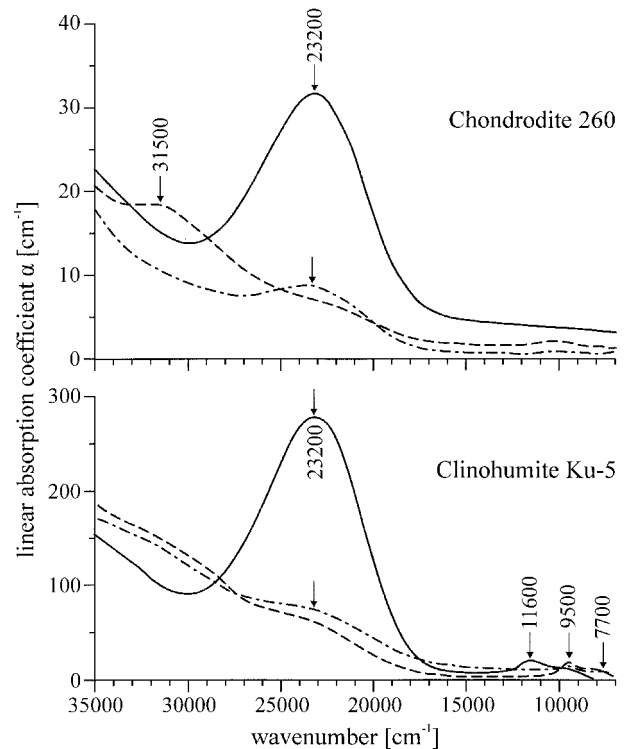

Fig. 1. Polarised electronic absorption spectra of chondrodite 260 and clinohumite Ku-5: Solid line = $\mathbf{E}||\mathbf{X}$, dot-dashed line = $\mathbf{E}||\mathbf{Y}$, dashed line = $\mathbf{E}||\mathbf{Z}$.

(i) An absorption edge in the UV at $\tilde{v} > 35000$ cm^{-1} which is polarised as
$\alpha_{E//Y} < \alpha_{E//Z} < \alpha_{E//X}$ in the spectra of chondrodites
$\alpha_{E//X} < \alpha_{E//Y} < \alpha_{E//Z}$ in the spectra of clinohumites
(ii) A broad ($\Delta\tilde{v}_{1/2} \approx 6000$ cm^{-1}) and weak band at 31500 cm^{-1} in the $\mathbf{E}||\mathbf{Z}$ spectra. It occurs as a shoulder ($\alpha \le 5$ cm^{-1}) in the $\mathbf{Z}$-spectra of clinohumite and is clearly discernible ($\alpha = 3$ cm^{-1}) at slightly higher energy in the $\mathbf{Z}$-spectrum of chondrodite.
(iii) A strong and broad band centered at 23200 cm^{-1} and strongly polarised with $\mathbf{E}||\mathbf{X}$ in spectra of all minerals studied. A weak, broad band at this energy occurs also in the $\mathbf{E}||\mathbf{Y}$ spectra. A very weak and broad shoulder near 23000 cm^{-1} in the $\mathbf{E}||\mathbf{Z}$ spectra (see Fig. 1) is possibly connected with a slight deviation from the exact orientation of the slabs on which the measurements were taken. Spectroscopic parameters of the most characteristic, intense and strongly polarised band at 23200 cm^{-1} in the spectra of all minerals studied are presented in Table 2.
(iv) A complex low-energy band system in the NIR: 11600 cm^{-1} in $\mathbf{E}||\mathbf{X}$ spectra, 9500 cm^{-1} in spectra with $\mathbf{E}||\mathbf{Z}$ and 7700 cm^{-1} in $\mathbf{E}||\mathbf{Y}$ and $\mathbf{E}||\mathbf{Z}$ spectra.

It is quite obvious that the broad, intense and strictly polarised band at 23200 cm^{-1} which is the dominating feature of the electronic absorption spectra of all the minerals studied here is in complete accordance with the basic criteria of metal-metal charge transfer, MM-CT, bands (Smith & Strens, 1976; Mattson & Rossman, 1987). The energy value of the band is close to those of Fe^{2+}-Ti^{4+} charge-transfer bands in the spectra of other Fe,Ti-bearing minerals with M-M dis-

Table 2. Contents of Fe and Ti, in atoms per formula unit, and spectroscopic parameters of the **X**-polarised CT-bands in the optical absorption spectra of the humite minerals studied.

Sample	Mineral	Contents of Fe and Ti, pfu		Parameters of CT-bands		
		Fe	Ti	$\tilde{\nu}$ [cm^{-1}]	α [cm^{-1}]	$\Delta\tilde{\nu}_{1/2}$ [cm^{-1}]
260	Chondrodite	0.0377	0.0083	23200	23.5	6000
15/84	Chondrodite	0.0698	0.0083	23200	16.8	5900
Kl-2	Clinohumite	0.022	0.217	23200	24.9	6200
SL-387	Clinohumite	0.796	0.058	23200	110	6000
Ku-5	Clinohumite	0.423	0.126	23200	290	6200
PS-92/94	Clinohumite	1.245	0.246	23150	600	5900
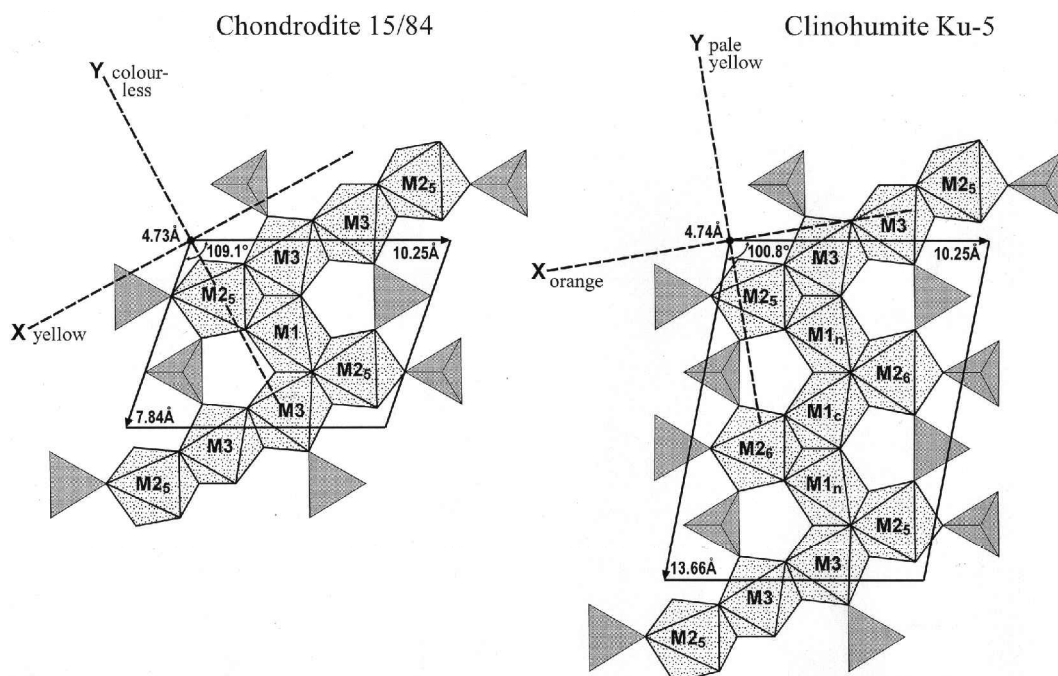
Fig. 2. Parts of the crystal structures of chondrodite (Gibbs *et al.*, 1970) and clinohumite (Robinson *et al.*, 1973), plotted after Ribbe (1980) to show the fragments of chains of edge-connected octahedra. Values of unit cell dimensions are quoted according to the results obtained in the present study by X-ray CCD methods on chondrodite 15/84 and clinohumite Ku-5. In all structural work since Bragg & West (1927) and Taylor & West (1928), $P2_1/b$ was used as space group to determine the structures of chondrodite and clinohumite, such that in the former a < c < b and in the latter a < b < c (*cf.* Jones, 1969). The orientation of the main axes of the optical indicatrices, **X**, **Y** and **Z**, with respect to the directions of the just mentioned unit cell dimensions are also plotted according to the results of the present work to show the relations between the optical indicatrices and the crystallographic axes.

tances between atoms in edge-sharing octahedra in the range 3.04–3.28 Å (Platonov *et al.*, 1991). Thus, it is justified to conclude that the band at 23200 cm^{-1} in the spectra of chondrodites and clinohumites is caused by Fe^{2+}-Ti^{4+} charge transfer.

The position of the MM-CT band in the blue-green range of the spectrum causes a dark-yellow, orange or red to reddish-brown colour of the humite minerals in **E**‖**X** polarisation. The hue, tone and saturation of the above colours depend on the intensity of the band in the spectra of each specific sample.

The pale-yellow or yellow colour of the mineral typical of the other polarisations, is mainly caused by the position of the absorption edge in the UV. In **E**‖**Y** polarisation, the

colour may be enhanced because the Fe^{2+}-Ti^{4+} CT-band exhibits a component in the **Y** direction (see below). In any case, the optical absorption study confirms the pleochroic scheme of the humite minerals: **X** > **Y** > **Z**.

As far as the problem of the Fe^{2+} and Ti^{4+} distribution in nonequivalent sites of the present low titanium chondrodites and clinohumites is concerned, it is to be considered that the charge-transfer interaction between Fe^{2+} and Ti^{4+} ions is principally possible within all types of fragments of edge connected octahedra in the two structures as depicted in Fig. 2. However, the fact also obvious from Fig. 2, that the structural methods (see above) proved the optical **X** vector to be parallel to M2$_5$M3M3M2$_5$ in chondrodite and subparallel, at an angle of about 19° to the same structural fragment in cli-
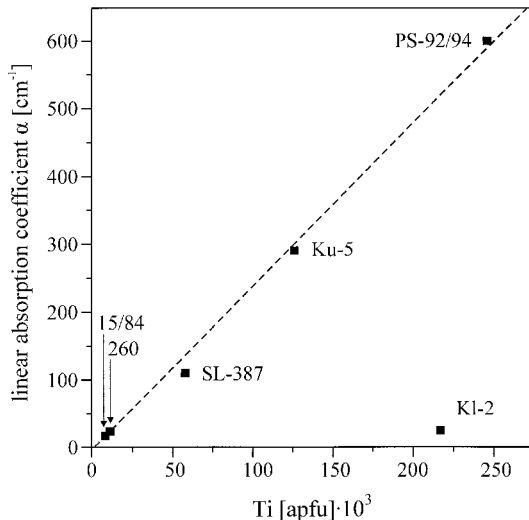
Fig. 3. Intensity, α [cm^{-1}], of the Fe^{2+}Ti^{4+} CT band at 23200 cm^{-1} in $\mathbf{E}||\mathbf{X}$ spectra of the humite minerals studied as a function of their titanium contents per formula unit (based on 2(F,OH) in all minerals). The strong deviation of the titanium-rich clinohumite Kl-2 from the linear regression shown as dashed line, is explained in the text.

nohumite, demonstrates that the Fe^{2+} and Ti^{4+} ions involved in the origin of the strong 23200 cm^{-1} CT-band are allocated in the interconnected octahedra of the M2$_5$M3M3M2$_5$ chain fragment. In consequence of the angle of about 19° between the MM-vector of that chain fragment and the optical $\mathbf{X}$ vector in clinohumite, a small part of the CT intensity should occur in $\mathbf{E}||\mathbf{Y}$ spectra of that mineral. This is indeed the case as the weak and broad band at 23000 cm^{-1} in $\mathbf{Y}$ polarisation (Fig. 1) shows. However, the same feature is also present in the $\mathbf{E}||\mathbf{Y}$ spectrum of chondrodite where it should not appear if charge-transfer interaction would exclusively occur in M2$_5$M3M3M2$_5$ exclusively. Possibly in both, chondrodites and clinohumites the weak CT-band at 23000 cm^{-1} in $\mathbf{E}||\mathbf{Y}$ is caused by charge transfer involving interconnected M3- and M1-type octahedra. This would correspond to the results by Platonov *et al.* (2001) on an unusually iron-rich clinohumite.

Fe-Ti charge transfer within the M2$_5$M3M3M2$_5$ structural fragments in both chondrodites and clinohumites, is consistent with both the allocation of the (OH,F)-ligands (*cf.* introduction) and with metal-metal distances. Low-charge ligands in edge-sharing octahedra enhance the overlapping of d-orbitals through the common edges, an effect that stabilizes Ti in M3. The M2$_5$-M3 distances were evaluated from our X-ray data as 3.24 Å in chondrodite 15/84 and 3.27 Å in clinohumite Ku-5 both well within the distance expected from the bands' position at 23200 cm^{-1} (see above). The slightly lower energy, 23000 cm^{-1}, of the weak $\mathbf{Y}$-polarised CT-band is in accordance with the slightly lower M3-M1 or M3-M1$_n$ distances 3.12 Å or 3.11 Å in chondrodite 15/84 or clinohumite KU-5, respectively. Thus, all evidence points to the allocation of titanium in the M3 sites of the minerals studied here.

The fact that in the present case of chondrodite and clinohumite spectra, the intensity of the MM-CT band observed in $\mathbf{E}||\mathbf{X}$, correlates strongly with the Ti^{4+} concentration

alone (Fig. 3) and only with a lower reliability on the concentration product of Ti^{4+} and Fe^{2+}, as obvious when comparing the correlations (1) and (2):

$$\alpha_{23200} = 2.4167 \cdot [\text{Ti}^{4+}]_{\text{pfu}} \quad r = 0.9967 \qquad (1)$$
$$\alpha_{23200} = 1.8248 \cdot [\text{Fe}^{2+}]_{\text{pfu}} \cdot [\text{Ti}^{4+}]_{\text{pfu}} \quad r = 0.9546 \qquad (2)$$

seems to be at variance with the results of Smith & Strens (1976) of a [Fe^{2+}]·[Ti^{4+}]-correlation for the FeTi-CT intensity. However, Smith & Strens' (1976) approach involves random distribution of the two ions in the structure under study. Indeed in this case, the probability to find iron and titanium in interconnected, neighbouring polyhedra depends on both the concentrations, [Fe^{2+}]$_{\text{pfu}}$ and [Ti^{4+}]$_{\text{pfu}}$. However, when there is non-random distribution, such that Ti^{4+} is – at least predominantly – present paired with Fe^{2+}, the MM-CT intensity is expected to correlate with [Ti^{4+}]$_{\text{pfu}}$ alone as long as [Ti^{4+}]$_{\text{pfu}} \leq$ [Fe^{2+}]$_{\text{pfu}}$ and will deviate from this correlation to too low intensity values when [Ti^{4+}]$_{\text{pfu}} \geq$ [Fe^{2+}]$_{\text{pfu}}$. Just this is observed in Fig. 3 (Kl-2, *cf.* Tab. 1). Thus, the results confirm correlation (1), involving non-random Fe^{2+}-Ti^{4+} distribution. This is further confirmed by the following consideration: Fe^{2+}-Ti^{4+} charge transfer is only possible when pairs of the two ions exist, be they randomly or non-randomly distributed and may they form isolated pairs or parts of extended clusters. Therefore, in the high-Ti clinohumite Kl-2, at maximum that part of Ti^{4+} pfu which is equivalent to Fe^{2+}, *i.e.* 0.022 pfu, will participate in the charge transfer. Hence, in the case of non-random distribution, the data point for Kl-2 should plot on the linear regression of Fig. 3, when using 0.022 Ti^{4+} as the abscissa value. This is really the case (*cf.* Fig. 3).

It might appear as if the close correlation α_{23200} = f([Ti]$_{\text{pfu}}$) might point to a band origin from dd-transitions of Ti^{3+}. However, this may be ruled out in the present case on the basis of the very broad band width, the nearly 100 % polarisation and the oscillator strengths calculated according to Smith & Strens (1976), *viz.* f$_{||}$ = 0.9 to 2.5*10^{-2} typical of charge-transfer transitions.

The broad band at 31500 cm^{-1} in $\mathbf{E}||\mathbf{Z}$ spectra of the present humite minerals (Fig. 1) was not observed in the electronic absorption spectra of olivines where strong and broad bands near 39800 cm^{-1} ($\mathbf{E}||\mathbf{Z}$ spectrum) and 34000 cm^{-1} ($\mathbf{E}||\mathbf{Y}$ spectrum) were found and interpreted as O→Fe CT-bands (Runciman *et al.*, 1973; Smith & Langer, 1981, 1982). Because in $P2_1/b$ $\mathbf{Z}$ is parallel to $\mathbf{a}$, the band at 31500 cm^{-1} as well as a complex low-energy band system in the NIR are connected obviously with properties of individual Fe-containing octahedral sites. A similar band near 29400 cm^{-1} was theoretically calculated from the strong UV absorption edge in $\mathbf{E}||\mathbf{Z}$ spectra of fayalites and was assigned to the O→Fe^{3+} charge-transfer band (Langer, 1988). It seems likely that the band at 31500 cm^{-1} is of the same nature and is connected with Fe^{3+} ions replacing Mg in the smallest M3 sites. If this is indeed the case, then from the intensities α_{31500} = 3 cm^{-1} for chondrodite or $\alpha_{31500} \leq$ 5 cm^{-1} for clinohumite (see above), site fractions of Fe^{3+} in the order of 10^{-5} to 10^{-4} may be estimated using the method of Dyar *et al.* (1996). Such small Fe^{3+} site fractions and their possible even smaller variations will definitely not influence the Fe^{2+}-Ti^{4+} MM-CT intensities. Moreover, any Fe^{2+}-Fe^{3+}

MM-CT which might be thought of if Fe^{3+} is ever present, will be so weak that it cannot be seen in our spectra. Indeed, there is no indication of a broad, very weak band around 13000 cm^{-1}, where $Fe^{2+}Fe^{3+}$ CT is expected in our **E||X** spectra (Fig. 1).

The band system in the NIR will not be thoroughly discussed as all details, band energies, intensity relations and polarisation dependencies, are analogous to those in olivine spectra (Burns, 1970). Thus, their origin from $^5T_2 \rightarrow {}^5E$ transitions of Fe^{2+} in M1 and M2$_{5,6}$ sites in the humites structures is obvious.

References

Bragg, W.L. & West, J. (1927): The structure of certain silicates. *Proc. Roy. Soc.*, **114**, 450–453.

Burns, R.G. (1970): Crystal field spectra and evidence of cation ordering in olivine minerals. *Am. Mineral.*, **55**, 1608–1632.

Deer, W.A., Howie, R.A., Zussman, J. (1982): Rock-forming Minerals, 2nd ed., vol. **1A**. Longman, London & New York.

Dyar, M.D., Kahlenberg, V., Langer, K., Terzenbach, H. (1996): Polarized single crystal spectra of natural and reheated olivines in the near ultraviolet spectral region and the problem of Fe^{3+}-bearing structural defects. *Phys. Chem. Minerals, 23*, 285–286.

Fujino, K. & Takeuchi, Y. (1978): Crystal chemistry of titanian chondrodite and titanian clinohumite of high pressure origin. *Am. Mineral.*, **63**, 535–543.

Gibbs, G.V., Ribbe, P.H., Anderson, C.B. (1970): The crystal structures of the humite minerals. II. Chondrodite. *Am. Mineral.*, **55**, 1182–1194.

Jones, N.W. (1969): Crystallographic nomenclature and twinning of the humite minerals. *Am. Mineral.*, **54**, 309–311.

Jones, N.W., Ribbe, P.H., Gibbs, G.V. (1969): The crystal chemistry of the humite minerals. *Am. Mineral.*, **54**, 391–411.

Kocman, V. & Rucklidge, J. (1973): The crystal structure of titanferrous clinohumite. *Can. Mineral.*, **12**, pt. 1, 39–45,

Langer, K. (1988): UV to NIR spectra of silicate minerals obtained by microscope spectrometry and their use in mineral thermodynamics and kinetics. *In* Salje, E.K.H., ed., Physical properties and thermodynamic behaviour of minerals. Reidel, Dordrecht, 639–685.

Larsen, E.S. (1928): The optical properties of the humite minerals. *Am. Mineral.*, **13**, 354–359.

Mattson, S.M. & Rossman, G.R. (1987): Identifying characteristics of charge transfer transitions in minerals. *Phys. Chem. Minerals,* **14**, 94–99.

Platonov, A.N., Langer, K., Matsyuk, S.S., Taran, M.N., Hu, X. (1991): Fe^{2+}-Ti^{4+} charge transfer in garnets from mantle eclogites. *Eur. J. Mineral.*, **3**, 19–26.

Platonov, A.N., Langer, K., Wildner, M., Polshin, E.V., Matsyuk, S.S. (2001): The crystal chemistry of the humite minerals: Spectroscopic studies and structure refinement of an unusual iron-rich clinohumite. *Z. Kristallogr.*, **216**, 154–164.

Ribbe, P.H. (1979): Titanium, fluoride, and hydroxyl in the humite minerals. *Am. Mineral.*, **64**, 1027–1035.

– (1980): The humite series and the Mn-analogs. *In* Ribbe, P.H., ed., Reviews in Mineralogy, 5. Orthosilicates. *Min. Soc. Amer.*, 231–274.

Ribbe, P.H. & Gibbs, G.V. (1971): Crystal structure of humite minerals. III. Mg/Fe ordering in humite and its relation to other ferromagnesian silicates. *Am. Mineral.*, **56**, 1155–1173.

Robinson, K., Gibbs, G.V., Ribbe, P.H. (1973): The crystal structures of the humite minerals. IV. Clinohumite and titanoclinohumite. *Am. Mineral.*, **58**, 43–49.

Runciman, W.A., Sengupta, D., Gourley, J.T. (1973): The polarized spectra of iron in silicates. II. Olivine. *Am. Mineral.*, **58**, 451–456.

Smith, G. & Langer, K. (1981): Polarized single-crystal near UV spectra of synthetic olivines. *Naturwiss.*, **67**, 373.

–, – (1982): Single crystal spectra of olivines in the range 40,000–5,000 cm^{-1} at pressures up to 200 kbar. *Am. Mineral.*, **67**, 343–348.

Smith, G. & Strens, R.G.J. (1976): Intervalence transfer absorption in some silicate, oxide and phosphate minerals. *In* Strens, R.G.J., ed., The Physics and Chemistry of Minerals and Rocks. Wiley Interscience Publ., New York, 584–612.

Taylor, W.H. & West, J. (1928): The crystal structure of the chondrodite series. *Proc. Roy. Soc.*, **117**, 517–532.

Tröger, W.E. (1971): Optische Bestimmung der gesteinsbildenden Minerale. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Winchell, A.N. & Winchell, H. (1951): Elements of Optical Mineralogy. 4th ed., Vol. **II**. Description of Minerals. John Wiley and Sons, New York.