Optical absorption spectra of Cr-bearing vesuvianite: detection and measurement of Cr^{3+} at the octahedral Y3-site

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ABSTRACT. — Polarised optical absorption spectra of six Cr-bearing vesuvianite single crystals have been measured at room temperature with the aim to define the Cr site occupancy and to quantify the molar extinction coefficients of spin-allowed electronic *d-d* bands in Cr^{3+}.

The crystals under study come from Nizjne Tagilsk, Russia. They were characterised by means of electron microprobe techniques, nuclear reaction analyses and Mössbauer spectroscopy. Cr-contents vary from 0.05-0.74 apfu and Fe^{3+}-concentrations are in the range 1.3-1.9 apfu. Boron as well as fluorine contents are low.

The optical absorption spectra display two dichroic spin-allowed Cr^{3+}-bands at ~16,500 (E>O) and ~23,000 cm^{-1} (O>E). Observed band polarisation and extinction coefficients in combination with previously published spectra obtained at elevated temperatures indicate that Cr^{3+} enters the Y3-site in vesuvianite. The absorption bands due to spin-allowed electron transitions in Cr^{3+} show a slightly skewed shape, which is attributed to splitting of the excited ^4F-states due to the low symmetry of the ligand field at the Y3-site. The crystal field splitting, 10Dq, and Racah B-parameters are determined to 16,500 (200) and 667 (13) cm^{-1}, respectively. These values are comparable to those reported for garnet group minerals, although

the B-value is slightly higher, which may be due to the presence of OH$^-$-ligands in addition to oxygen ligands at the Y3-site of vesuvianite.

Determined molar extinction coefficients (ε) for the two spin-allowed Cr^{3+}-bands at ~16,500 and ~23,000 cm^{-1} are 15 (E∥O), 26 (E∥E) and 24 (E∥O), 16 (E∥E) l·mol^{-1}·cm^{-1}, respectively. Linear regression analyses of intensity data in combination with detailed spectrum analysis show that a substantial overlap of narrow spin-forbidden absorption bands due to electronic transitions in Fe^{3+} at the Y3-site makes intensity data obtained from the Cr^{3+}-band at ~23,000 cm^{-1} less suitable for analytical purposes. However, the relatively high ε-value (15 l·mol^{-1}·cm^{-1}) calculated for the Cr^{3+}-band at ~16,500 cm^{-1} in E∥O allows detection of Cr^{3+} in unoriented vesuvianite crystals in, e.g., petrographic thin sections at concentration levels of 0.25 wt% Cr_2O_3 or higher. As the detection limit is inversely proportional to the sample thickness it may be considerably improved provided larger (>30 μm) crystals are available.

RIASSUNTO. — Allo scopo di definire l'occupanza di sito del cromo e quantificare i coefficienti di estinzione molare delle bande *spin-allowed d-d* nel Cr^{3+}, sono stati misurati gli spettri di assorbimento ottico polarizzati a temperatura ambiente su sei cristalli di vesuvianite cromifera.

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I cristalli studiati, provenienti da Nizjne Tagilsk (Russia), sono stati caratterizzati tramite microsonda elettronica, analisi di reazione nucleare e spettroscopia Mössbauer. I contenuti di Cr variano da 0,05 a 0,74 atomi per unità di formula e le concentrazioni del Fe^{3+} oscillano tra 1,3 e 1,9 atomi per unità di formula; i contenuti di B e F sono bassi.

Gli spettri di assorbimento ottico evidenziano due bande distinte *spin-allowed* di Cr^{3+} a 16500 (E>O) e 23000 cm^{-1} (O>E). La banda di polarizzazione osservata ed i coefficienti di estinzione unitamente agli spettri già pubblicati ottenuti a temperature elevate indicano che il Cr^{3+} occupa il sito Y3 della vesuvianite. Le bande di assorbimento dovute alla transizione elettronica *spin-allowed* nel Cr^{3+} mostrano una forma leggermente asimmetrica attribuibile allo sdoppiamento degli stati eccitati ^4F dovuto alla bassa simmetria del campo dei ligandi nel sito Y3. Lo sdoppiamento del campo cristallino 10Dq ed i parametri B di Racah sono stati determinati rispettivamente a 16500 (200) e 667 (13) cm^{-1}. Questi valori sono paragonabili a quelli riportati per i minerali del gruppo dei granati sebbene il valore di B sia leggermente superiore; ciò potrebbe essere dovuto alla presenza di gruppi OH^- oltre all'ossigeno nel sito Y3 della vesuvianite.

I coefficienti di estinzione molare (ε) per le due bande *spin-allowed* del Cr^{3+} a 16500 e 23000 cm^{-1} sono rispettivamente 15 (E∥O), 26 (E∥E) e 24 (E∥O), 16 (E∥E) $l·mol^{-1}·cm^{-1}$. Analisi di regressione lineare dei dati di intensità combinati con un'analisi dettagliata dello spettro, mostrano un'evidente sovrapposizione di sottili bande di assorbimento *spin-forbidden* dovute a transizioni del Fe^{3+} nel sito Y3, e rendono i dati di intensità ottenuti per la banda Cr^{3+} a 23000 cm^{-1} poco adatti ai fini analitici. Tuttavia i valori relativamente elevati di ε (15 $l·mol^{-1}·cm^{-1}$) calcolati per la banda del Cr^{3+} a 16500 cm^{-1} a E∥O consentono il riconoscimento di Cr^{3+} in cristalli non orientati di vesuvianite, ad esempio in sezioni sottili petrografiche per livelli di concentrazione di 0,25% o maggiori di Cr_2O_3. Poiché il limite di rivelabilità è inversamente proporzionale allo spessore del campione, lo stesso può essere migliorato qualora fossero disponibili cristalli piu grandi.

KEY WORDS: *Vesuvianite, chromium, optical absorption spectroscopy, microprobe analysis, Mössbauer spectroscopy.*

INTRODUCTION

Vesuvianite is a common rock-forming silicate mineral in various metamorphic settings. Structurally and chemically it is far more complex than the structurally related garnet group minerals. The true symmetry as well as the chemical formula of vesuvianite have been subjects for extended debates. During the last decade a large number of research papers have been dedicated to these questions. Groat *et al.* (1992), formulated on the basis of chemical and structural work on a large set of samples, a new general formula, $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, which also considered B-incorporation at the special T-sites. Later, Groat *et al.* (1994a, b), could show by means of combined structural refinements and chemical analyses that a small number of vesuvianites may have Y-cations exceeding 13 apfu, which was explained by the presence of an additional T-site. Following the vesuvianite site nomenclature as proposed by Groat *et al.* (1992) and subsequently modified (Groat *et al.*, 1994a, b), the total number of unique cation sites in the vesuvianite structure equals 12, distributed as 4 X-sites, 3 Y-sites, 3 Z-sites and 2 T-sites. The X-sites are normally occupied by Ca and other larger cations of low charge, while small cations of high charge, as e.g. Si, occupy the Z-sites. Cations of intermediate character with respect to size and charge, as e.g. the cations of the first transition element series as well as Al and Mg, occupy the Y-sites. T-sites are normally the loci for boron, but also to some extent, as demonstrated by Groat *et al.* (1994a), for Al and Fe. The T-sites may be unoccupied. The structure further constrains the occupancy of the X4- and Y1-sites to a maximum of 50%.

The three unique Y-sites display distinctly different characters, which in turn rule the site distribution of transition metal cations in vesuvianite. The Y1-site is a square pyramid with an axis of rotation (C_4) coinciding with the crystallographic c-axis. The octahedral Y2-site is the smallest of the Y-sites and the rotation axis (C_2) is at an angle of ~65° to the

c-axis. Finally, the six-coordinated Y3-site is characterised by intermediate M-L bond distances and it is of the lowest point symmetry (C_1). The multiplicity of these three sites is 1, 4 and 8, respectively.

The distribution of some transition metal cations among the Y-sites in vesuvianite has been successfully solved by means of X-ray diffraction techniques. For instance, the virtually complete ordering of Cu^{2+} at the five-coordinated Y1-site has been nicely demonstrated by Fitzgerald *et al.* (1986). However, the complexity in terms of chemistry and specifically transition metal chemistry which natural vesuvianite usually exhibit makes occupancy determinations by diffraction methods occassionally less viable. So far, the only indication of Cr-distribution in vesuvianite is based on band assignments made on optical absorption spectra obtained on a single vesuvianite crystal (Platonov *et al.*, 1993). Low concentrations of Cr in natural vesuvianite in combination with substantial amounts of ferric iron, which has identical charge and similar cation size as Cr^{3+}, present limitations for accurate determinations of Cr^{3+} site distribution by means of diffraction methods.

The spectra obtained by Platonov *et al.* (1993) were interpreted on the basis of the retrieved crystal field splitting parameter, 10Dq, for Cr^{3+} and temperature dependence of the recorded spin-allowed absorption bands due to Cr^{3+}. They concluded that the obtained parameters agreed with Cr^{3+} ordered at the octahedral Y3-site.

In the present study several single crystals of vesuvianite showing a range of Cr-contents have been investigated with the aim to evaluate the proposed (Platonov *et al.*, 1993) distribution scheme for Cr^{3+}. An additional object of the study has been to evaluate the possibility to apply optical absorption spectroscopy as a probe technique for quantitative Cr-determinations in vesuvianite. As a consequence of these two aims, the retrieval of band intensity data is at the focus of this spectroscopic study.

SAMPLES AND METHODS

All the present samples originated from Nizjne Tagilsk, the Urals, Russia. The vesuvianite crystals are anhedral to subhedral and attain a maximum size of 5 mm. The mineral is coloured in shades of green and occurs together with calcite and pink coloured chlorite as infillings in mm- to cm-sized fractures in a dense chromite-rich matrix. Under the microscope the vesuvianite crystals are distinctly pleochroic displaying a yellowish green colour for E||O (= E⊥c) and a bluish green colour for E||E (= E||c).

For the present study a large number of vesuvianite single crystals showing a variable colour intensity were preselected from four different samples (NRM#882795, #882811, #221093 and #221142) of the mineral collection at the Swedish Museum of Natural History. These crystals were individually oriented under the polarising microscope using conoscopic illumination. By applying Mallard's method, crystal orientations were determined to be correct within at least 5 degrees, which implies that errors in absorbance values introduced by any misalignments are less than 1%. All crystals were ground and polished on two parallel sides producing self-supporting single crystal absorbers. The absorbers were chemically analysed and a final selection of crystal absorbers for the absorption study was made on the basis of chemical composition as well as chemical and optical homogeneity. The preselected crystals from samples #221093, #882795 and #882811 were each of almost identical composition and they showed negligible chemical heterogeneity, while crystals from sample #221142 displayed variable Cr-, Al- and Fe-contents and some of them showed compositional zoning. The final crystal selection consequently included one crystal each from the first three samples and additionally three chemically homogeneous crystals with different Cr-contents from sample #221142. The single crystal absorber thickness varied depending on original crystal size and Cr-content from 145 to 440 μm.

The concentration of the heavier elements (Z=9) of the selected crystals was determined by electron microprobe techniques, using a Cameca SX50 instrument operated at 20 kV accelerating potential and 12 nA sample current. The standard materials used were albite (Si), Al_2O_3 (Al), MgO (Mg), $MnTiO_3$ (Mn, Ti), Fe_2O_3 (Fe), wollastonite (Ca), Cr_2O_3 (Cr), and vanadinite (V). Wavelength dispersive scans revealed no detectable amounts of any other elements including fluorine. The detection limit for F is estimated to be 0.4 wt%. Raw data were reduced by means of the ZAF-related PAP-program (Pouchou and Pichoir, 1984). Sample formulae were calculated on basis of 50 cations per formula unit and H_2O-contents were calculated on the basis of charge neutrality and 78 anions per formula unit.

The possible incorporation of boron in the present samples was evaluated by means of particle induced nuclear reaction analyses (NRA) utilising the nuclear reaction $^{11}B(p, 2\alpha)^4He$, which has a broad resonance cross-section peaking at 660 keV (Moncoffre, 1992). For the present boron analysis of sample NRM #882811 the current was kept at 200 pA with a beam spot size of 4 μm. The NRA data were acquired in the form of a map using a 128 × 128 grid with a step size of 4 μm. As a standard served a well characterised and homogeneous tourmaline sample (NRM # 600235) containing 10.18 wt% B_2O_3. In the present experimental standard set-up, the estimated detection limit and relative error of the B-analyses are 10 ppm and 5-10%, respectively. To evaluate the B-concentrations, a polygon window tracing the crystal outline was defined and corresponding boron signal and ion charge data were extracted. In this way normalised boron yields were obtained, which were evaluated with respect to the yield recorded for the boron standard to obtain quantitative B-analyses. In order to estimate the total background contribution (pile-up effects in the particle detector and additional nuclear reactions emitting high-energy particles), spectra of a virtually boron-free quartz crystals were recorded. This background contribution was accounted for in the B-analysis.

A Mössbauer spectrum of sample NRM#882811 was recorded at ambient conditions with a constant acceleration system working in conjunction with a 1024 channel MCA using a nominal 50 mCi $^{57}Co/Rh$ source and a gas-filled proportional counter as detector. A pressed flat circular disc of a homogenised mixture of 54 mg mineral powder and 75 mg transoptic polymer powder was used as sample absorber. A thin foil of metallic iron (α-Fe) was used for velocity calibration and consequently all reported Mössbauer parameters are given relative to α-Fe at room temperature. A fit of the recorded spectrum was carried out using a computer program (Jernberg and Sundqvist, 1983) assuming Lorentzian line shapes and equal values of FWHM (full width at half maximum) and intensity of the two components of each quadrupole doublet.

Room-temperature polarised optical absorption spectra of the present Cr-bearing vesuvianites were recorded with a Zeiss MPM 800 single beam microscope spectrometer using a 75 W Xenon arc lamp and a 100 W tungsten lamp as light source in the UV-VIS region (350-800 nm) and the NIR region (800-2100 nm), respectively. A photomultiplier and a photoconductive PbS-cell served as detectors in the two respective spectral regions. Concave holographic gratings were used as monochromators and an UV-transparent Glan-Thompson prism served as polariser. UV-transparent (Zeiss Ultrafluar 10×) lenses were used as objective and condenser throughout the entire wavelength region. The diameter of the measuring spot was equal to 40 μm in all experiments. The crystal spots used for absorption spectra recordings were identical to those covered by a set of electron microprobe analyses. All recorded spectra were analysed by means of peak deconvolution using the Jandel PeakFit 4 program under the assumption of Gaussian peak shapes and an UV-background absorption of exponential shape.

RESULTS

The chemistry of the present vesuvianite samples is summarised in Table 1. They are with the exception of the Cr-content, which varies betwen 0.05 and 0.68 apfu, and the somewhat lower Al-content in the main stream of vesuvianite compositions as reported by Groat *et al.* (1992).

It has been shown that B may be a major chemical component in vesuvianite attaining concentrations of approximately 3 apfu (Groat *et al.*, 1994b). To evaluate the B-content of the present samples a NRA-analysis of sample #882811 was carried out. This analysis showed that this crystal was homogeneous also with respect to B and that the B-content was as low as 121 ± 16 ppm. This low B-content is consistent with the reported (Groat *et al.*, 1992) relationship between B-concentration and Al-, Mg- and OH-content in vesuvianite. As the

additional five Cr-bearing vesuvianite crystals originate from the same geological environment and are comparable with respect to Al- and Mg-concentrations it is reasonable to assume that they are also very low in boron.

The valence state of iron is an important factor influencing the optical properties of vesuvianite. Examples of cooperative absorption processes involving, e.g., ferrous iron have been documented in vesuvianite spectra (Manning, 1975 and Manning, 1976). A Mössbauer spectrum of sample #882811 was recorded at room temperature in order to obtain information on the iron valency and the location of iron in the present samples. The resulting spectrum is illustrated in fig. 1, which also shows the result of the fitting procedure. A slight assymetry, which is not fully accounted for by the simple fitting model used (two quadrupole doublets), is probably in part due to

TABLE 1

Electron microprobe analyses of Cr-bearing vesuvianite.

| Sample #	882811	882795	221093	221142a	221142b	221142c
SiO_2 (wt%)	36.52	36.18	36.26	35.88	36.39	35.77
Al_2O_3	14.59	14.78	14.36	13.94	15.08	15.12
TiO_2	0.05	0.48	0.08	0.82	0.18	0.17
Fe_2O_3	3.59	4.36	4.23	4.39	4.92	5.05
MnO	0.01	0.00	0.00	0.03	0.00	0.00
Cr_2O_3	1.74	0.60	1.89	0.98	0.39	0.12
V_2O_3	0.03	0.00	0.00	0.03	0.03	0.00
MgO	3.28	3.78	3.22	3.62	3.42	3.32
CaO	36.27	36.25	35.85	36.00	36.34	35.95
H_2O_{calc}	2.91	3.03	2.85	2.94	2.96	2.95
SUM	98.98	99.46	98.74	98.62	99.71	98.43
Atoms on the basis of 50 cations per formula unit						
Si	17.97	17.70	17.93	17.76	17.78	17.70
Al	8.46	8.52	8.37	8.14	8.68	8.81
Ti	0.02	0.18	0.03	0.30	0.07	0.06
Fe^{3+}	1.33	1.61	1.57	1.63	1.81	1.88
Mn	0.01	0.00	0.00	0.01	0.00	0.00
Cr	0.68	0.23	0.74	0.38	0.15	0.05
V	0.01	0.00	0.00	0.01	0.01	0.00
Mg	2.41	2.76	2.37	2.67	2.49	2.45
Ca	19.12	19.00	18.99	19.09	19.02	19.05
OH_{calc}	9.55	9.88	9.40	9.71	9.66	9.74
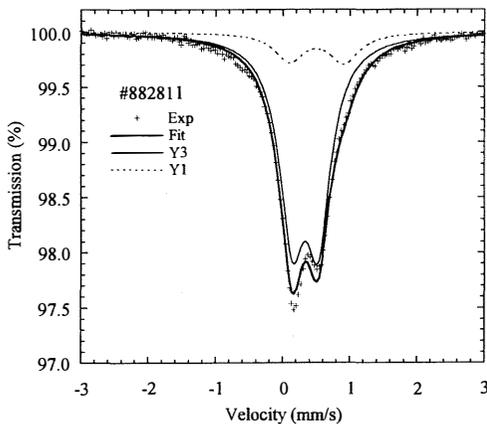
Fig. 1 – Room temperature ^{57}Fe Mössbauer spectrum of sample NRM #882811. Experimental data are shown as small crosses, while the fit total spectrum is depicted as a bold solid line. The two fit subspectra due to Fe^{3+} at the Y1- and Y3-site are illustrated by the thin dotted and solid lines, respectively.

distribution effects caused by variable next-nearest neighbour environments for Fe^{3+}. The two fit quadrupole sets contributing to the recorded spectrum are characterised by the following hyperfine parameters: CS (centroid shift) = 0.33 mm/s, QS (quadrupole splitting) = 0.39 mm/s and CS=0.52 mm/s, QS=0.81 mm/s, respectively. The relative intensity of the two quadrupole sets are 88 and 12% and FWHM-values are 0.41 and 0.49 mm/s, respectively.

The optical absorption spectra of the present samples display a general structure similar to the previously reported (Platonov *et al.*, 1993) spectra of one Cr-bearing vesuvianite crystal. The present spectra are characterised by a pleochroic (E>O) UV-absorption edge, which extends well into the visible spectral region. Superimposed on this edge there occur two relatively broad, intense and pleochroic bands at ~23,000 cm^{-1} (O>E) and ~16,500 cm^{-1} (E>O). Additional narrow and relative weak bands are observed at approximately 26,000, 24,000, 21,600, 19,300, 15,070, 14,500, 14,360, 14,260 and 7,150 cm^{-1}. The position of the two strong bands varies with polarisation and particularly in the E‖O-spectra they display a slightly asymmetric shape (fig. 2), which

becomes more pronounced in spectra of the Cr-poor samples (fig. 3). This feature may indicate that there are two or more closely spaced major absorption bands contributing to each of these two peaks. Figure 3 illustrates qualitatively the decrease in intensity of the two major peaks in spectra of the present six samples with decreasing Cr-content.

Different band resolution models were used to derive quantitative spectral parameters for the observed major absorption bands. As a first approximation an unconstrained fitting model including only two main absorption bands in addition to the UV-edge absorption function was applied. In this procedure the resulting band widths of the two major peaks became relatively large (2,600 - 3,500 cm^{-1}), with the larger band widths for the high-energy peak at 23,000 cm^{-1} (fig. 4). In an alternative model, two partly overlapping bands were assumed to contribute to each of the two major absorption peaks. In this fitting procedure convergence was not reached and resulting band widths, peak positions and band intensities varied in a highly irregular manner. In addition to this, the difference in position between the two components of each major absorption region became in most cases smaller than half the fit
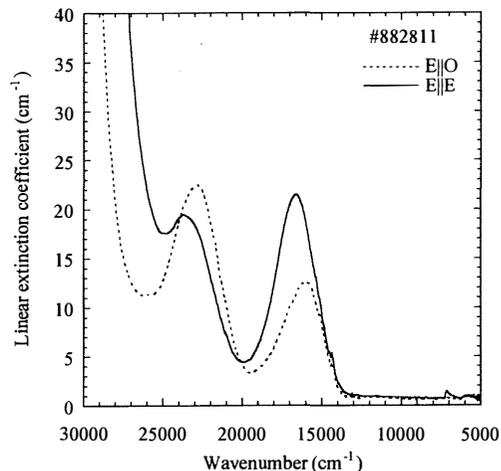

Fig. 2 – Polarised optical absorption spectra (E‖O and E‖E) of vesuvianite sample NRM #882811, illustrating the dichroic character as well as the skewed band shapes of the two spin-allowed *d-d* bands due to Cr^{3+}.

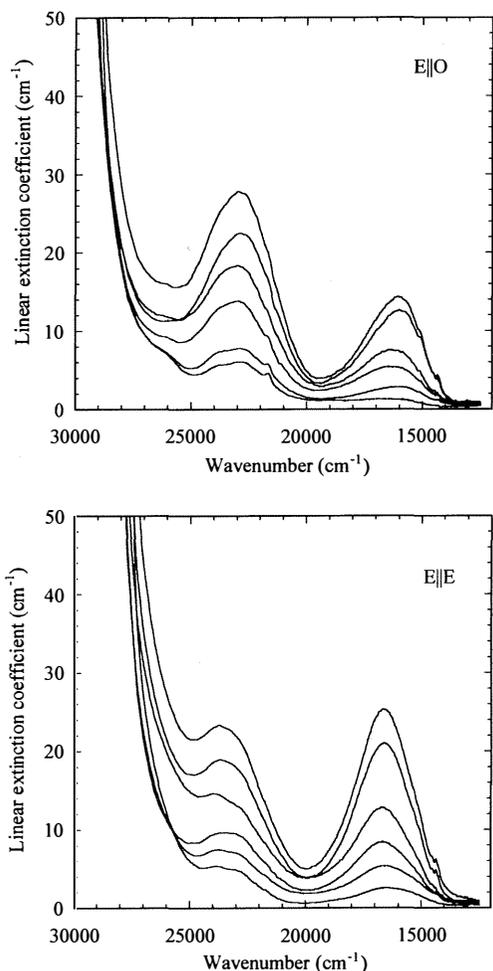quantitative positive correlations between the recorded absorption coefficient of the two major absorption bands and the Cr-concentration of the vesuvianite crystals. The obtained regression data for the band at 16,500 cm^{-1} in E‖O and E‖E are α $(cm^{-1}) = 0.118 + 17.4$ C_{Cr} (apfu), $(r^2=0.994)$, and $\alpha = 0.253 + 30.0$ C_{Cr}, $(r^2=0.994)$, respectively. For the

Fig. 3 – Polarised optical absorption spectra of the investigated six single crystals (top, E‖O and bottom, E‖E) in the spectral range for the spin-allowed Cr^{3+}-bands. Illustrated spectra are in decreasing order of absorption recorded from samples #221093, #882811, #221142a, #882795, #221142b and #221142c, respectively.

band widths. In summary, this indicates that a unique solution of the spectra using the second approach can not be obtained unless a number of arbitrary constraints are introduced. Consequently, the results of the spectrum deconvolution as reported in Table 2 are based on the unconstrained fitting model.
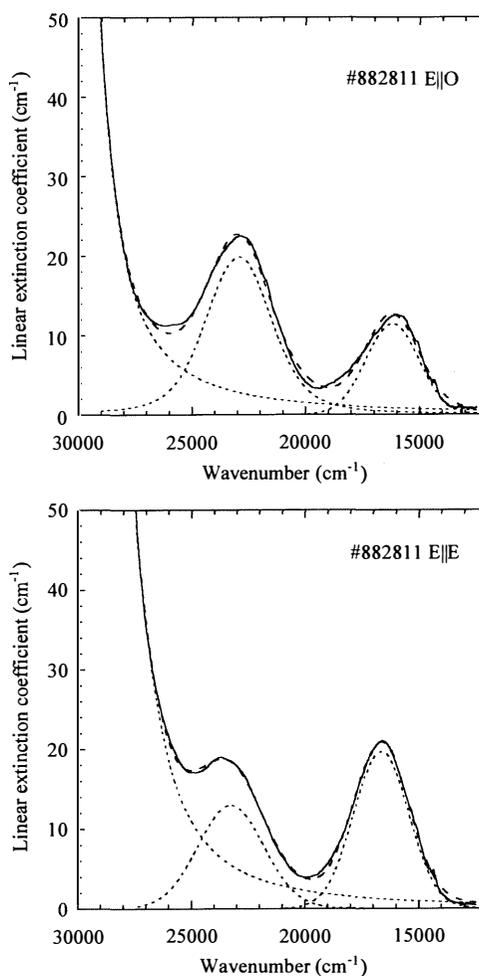
As illustrated in fig. 5, there exist excellent

Fig. 4 – Computer resolved polarised absorption spectra of sample NRM #882811 (top, E‖O and bottom, E‖E). Bold solid lines represent the measured spectra, while dotted lines illustrate the results of the band deconvolution procedure assuming Gaussian band shapes and an exponential UV-background contribution.

TABLE 2

Sample thickness, properties of Cr^{3+}-bands and crystal field parameters.

Sample NRM #	Thickness (μm)	ν_1 (cm^{-1})	α_1 (cm^{-1})	$FWHM_1$ (cm^{-1})	ν_2 (cm^{-1})	α_2 (cm^{-1})	$FWHM_2$ (cm^{-1})	10Dq (cm^{-1})	B (cm^{-1})
E∥O									
#221093	160	16.243	12.9	2.622	22.996	23.6	3.457	16.243	685
#882811	223	16.192	11.4	2.733	22.946	19.9	3.433	16.192	685
#221142a	145	16.405	6.5	2.686	23.098	15.2	3.511	16.405	674
#882795	226	16.421	4.5	2.961	23.116	11.5	3.358	16.421	674
#221142b	440	16.372	2.1	2.685	23.063	6.1	3.245	16.372	674
#221142c	438	16.348	0.6	2.823	22.938	3.5	3.412	16.348	661
E∥E									
#221093	160	16.619	23.5	2.841	23.302	15.2	3.336	16.619	669
#882811	223	16.641	19.7	2.845	23.255	12.9	3.426	16.641	660
#221142a	145	16.711	11.2	2.823	23.267	7.7	3.477	16.711	651
#882795	226	16.682	7.5	2.940	23.258	6.6	3.327	16.682	654
#221142b	440	16.620	4.7	3.196	23.273	4.5	3.441	16.620	665
#221142c	438	16.706	1.9	2.849	23.210	1.8	3.321	16.706	645

absorption band at 23,000 cm^{-1} the resulting relations in E∥O and E∥E are $\alpha = 3.29 + 26.9$ C_{Cr}, ($r^2=0.958$), $\alpha = 1.52 + 17.7$ C_{Cr}, ($r^2=0.980$), respectively. Taking into account that the correlations should be constrained to pass through the origin, molar extinction coefficients for the Cr-related absorption bands at 23,000 cm^{-1} and 16,500 cm^{-1} are calculated from these regression equations to be 24 (E∥O), 16 (E∥E) and 15 (E∥O), 26 (E∥E) $l\cdot mol^{-1}\cdot cm^{-1}$, respectively.
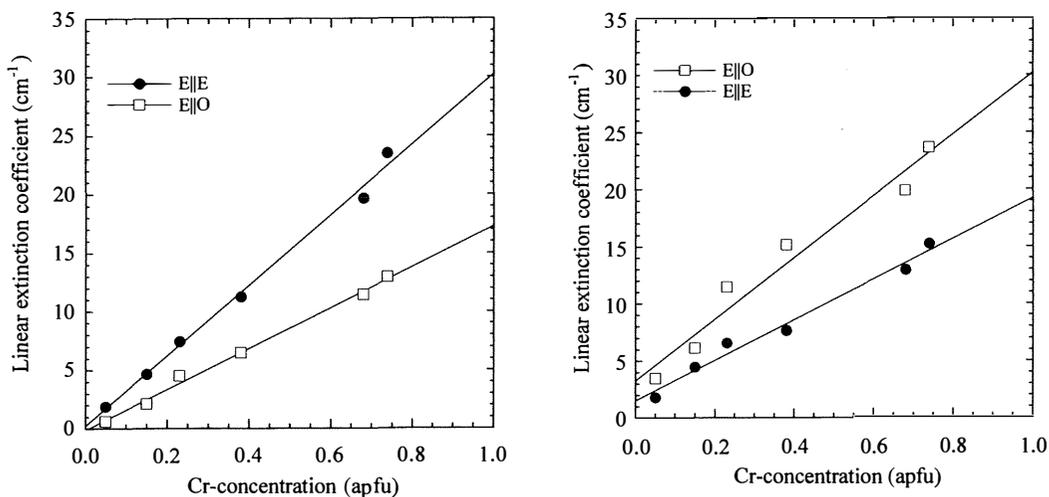

Fig. 5 – Linear regression analyses of thickness normalised intensity data (α) for the two spin-allowed Cr^{3+} -bands and sample Cr^{3+} concentration. The figure to the left illustrates the data obtained for the ν_1-band at ~16,500 cm^{-1} and the right-hand figure the results for the ν_2-band at ~23,000 cm^{-1}. Solid lines represent obtained regression fits.

DISCUSSION AND CONCLUSIONS

Chemistry and Mössbauer spectroscopy

The electron microprobe analyses of the present samples show that chromium and iron are the only elements present at sufficiently high concentration levels to produce significant electronic *d-d* bands in optical absorption spectra. As iron may be present in the divalent as well as in the trivalent state in vesuvianite and thus give rise to absorption bands of highly different character, it is essential to obtain an independent characterisation of the iron valency in the present samples. From the centroid shift (CS) hyperfine parameter of the two resolved quadrupole doublets in the recorded Mössbauer spectrum it is evident that iron occurs in the trivalent state. The low CS-values, 0.33 and 0.52 mm/s, are in the range of centroid shifts recorded for Fe^{3+} in a large number of silicate minerals (Coey, 1984), but they are distinctly lower than CS-values recorded for Fe^{2+} at sites coordinated by five or more ligands.

Published Mössbauer spectra of vesuvianite samples with no or neglectable contents of ferrous iron (Manning and Tricker, 1975, Olesch, 1979 and Tricker *et al.*, 1981) reveal two quadrupole doublets characterised by hyperfine parameters (CS=0.29-0.35, QS=0.42-0.56 mm/s and CS=0.40-0.62, QS=0.82-1.12 mm/s), which are similar to those recorded for the present sample #882811. The doublet characterised by the lower centroid shift and quadrupole splitting (QS) has been assigned to ferric iron at the Y3-site, but the assignment of the second doublet is more ambiguous. Tricker et al. (1981) argued that this second low-intensity resonance doublet is due to Fe^{3+} at the eight-coordinated X4-site, while Olesch assigned this particular absorption doublet to Fe^{3+} at the five-coordinated Y1-site. Except for the assignment proposed by Tricker *et al.* (1981) no additional evidence for ferric iron entering the vesuvianite X4-site have been presented in literature. In fact, single crystal EPR-spectroscopy (Rager and Zabinski, 1995) indicate that ferric iron may enter the five-coordinated Y1-site in substantial amounts, which supports the assignment proposed by Olesch (1979). Irrespective of the detailed ferric iron site occupancy it may be concluded from the present Mössbauer spectrum that iron is present in the trivalent state and that there exists no evidence for the presence of ferrous iron. Furthermore, approximately 90% of the ferric iron is located at the six-coordinated Y3-site.

Optical spectroscopy and band assignments

The recorded optical absorption spectra show a band structure in common for Cr^{3+}-bearing substances, in which Cr^{3+}-ions are six-coordinated to oxygen or hydroxyl anions. In these spectra, two relatively intense spin-allowed bands marking the transitions between the ground state and the excited states $^4T_{2g}(F)$ and $^4T_{1g}(F)$ occur at energies between approximately 15,000-19,000 cm^{-1} and 21,500-25,500 cm^{-1}, respectively (e.g. Burns, 1993). This general observation, in combination with the presently demonstrated correlation between band intensity and Cr-content, supports the previously proposed assignments (Platonov *et al.*, 1993) of the band at ~16,500 cm^{-1} (v_1) to the spin-allowed electronic transition $^4A_{2g}(F)$ $\rightarrow$$^4T_{2g}(F)$ and the band at ~23,500 cm^{-1} (v_2) to the spin-allowed transition $^4A_{2g}(F)$ $\rightarrow$$^4T_{1g}(F)$ in six-coordinated Cr^{3+}.

The asymmetric peak form as well as the anomalously large apparent band widths of the two spin-allowed Cr^{3+}-bands may be due to partial overlap of two or more absorption bands in the two spectral regions, respectively. This in turn may be related to a further split of the excited spectroscopic F-states of Cr^{3+} as a consequence of low crystal field symmetry at the Cr-bearing site. Alternatively it may be ascribed to a distribution of Cr^{3+} over a number of unequal structural sites.

In vesuvianite there are three sites (Y1-Y3), which on the basis of cation size arguments may be occupied by Cr^{3+}. Provided that Cr^{3+} is fully ordered at one of these sites, the observed d-d band asymmetry constrains the possible cation location. Due to the coinciding
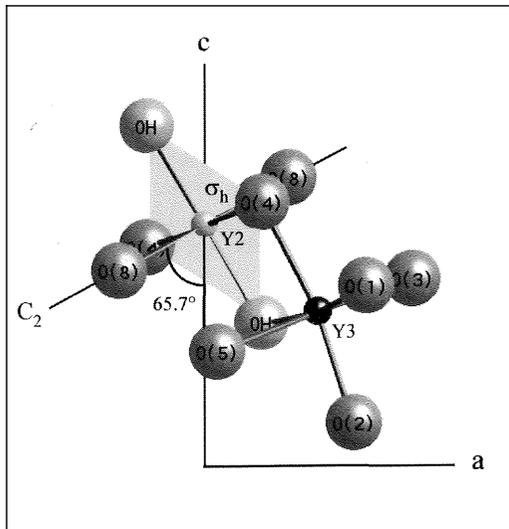
Fig. 6 – Ball and stick model of the Y2- and Y3-site of the vesuvianite structure. Existing symmetry elements of higher order (C_2-axis and the mirror plane σ_h) have been delineated for the Y2-site and their geometric relations to the crystallographic axes are also depicted.

crystallographic c-axis, optical E-direction and the C_4-axis of the Y1-site (C_{4v}-symmetry), spin-allowed d-d bands related to Cr^{3+} at this site are predicted to be completely polarised along E or O. Consequently bands showing apparent asymmetric shapes due to closely spaced bands marking transitions to split excited F-states will not be observed for Cr^{3+} at the Y1-site. Taking into account electronic dipole transition probabilities as well as vibronic coupling effects, the inferred term split and resulting apparent band skewness is, however, in keeping with Cr^{3+} occupying Y2- or Y3-sites.

The major symmetry difference between the Y2- and the Y3-site is the presence of a centre of symmetry for the Y2-site. The point symmetry of the Y2-polyhedron is to a first approximation C_{2h} and its C_2-axis is at an angle of ~65° to the optical E-direction (fig. 6), while the Y3-site is of C_1-symmetry and possesses only the identity (E) symmetry element. Previous spectroscopic studies (e.g. Taran *et al.*, 1994) on a large number of other Cr^{3+}-

bearing minerals have clearly demonstrated how the intensity of spin-allowed Cr^{3+} d-d bands depends on the symmetry of the coordination site. For spectra of minerals in which Cr^{3+} is located at sites possessing symmetry centres, the molar extinction coefficient sums ($\varepsilon_X + \varepsilon_Y + \varepsilon_Z$) of the spin-allowed Cr^{3+} v_1- (or U-) band were found to be in the range 15-25 l·mol^{-1}·cm^{-1}. When located at low symmetry sites without symmetry centres the corresponding values ranged from 40-70 l·mol^{-1}·cm^{-1}. The molar extinction sum for the Cr^{3+} v_1-band at ~16,500 cm^{-1} in the present vesuvianite spectra is 56 l·mol^{-1}·cm^{-1}, which indicate that Cr^{3+} is located at a site lacking a centre of symmetry. In addition to this Taran *et al.* (1994) demonstrated that the band intensity of the spin-allowed d-d bands due to Cr^{3+} in centrosymmetric sites increased on increasing temperature, while the intensity of bands due to Cr^{3+} in the low-symmetry site (C_1) of topaz were unaffected by temperature changes. The intensity of the corresponding bands in spectra of the vesuvianite crystal studied by Platonov *et al.* (1993) remained almost constant in the temperature range 77-800 K. Consequently, the present molar extinction coefficient data for the spin-allowed Cr^{3+} d-d bands, as well as the restricted temperature data indicate that Cr^{3+} is, as proposed by Platonov *et al.* (1993), preferentially located at the Y3-site in vesuvianite.

In addition to the spectroscopic indications for Cr^{3+} occupancy of the Y3-site in vesuvianite, a large number of single crystal refinements of vesuvianite of various composition show that the Y2-site is almost exclusively occupied by Al, while major cation substitutions take place at the Y3- and Y1-sites. So far there exists no structural refinement of Cr^{3+}-rich vesuvianite, but studies performed on a number of samples with Fe- and Mg-contents comparable to the present ones show complete Al-occupancy at the Y2-site, while Y1 and Y3 sites are occupied by Al, Mg and Fe in various amounts (Rucklidge *et al.*, 1975, Giuseppetti and Mazzi, 1983 and Ohkawa *et al.*, 1992). In
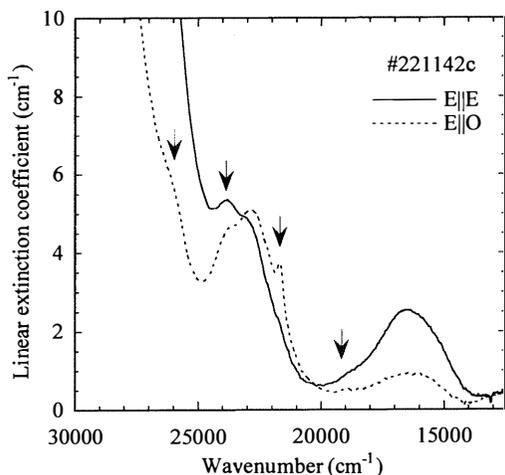
Fig. 7 – Polarised optical absorption spectra of the Cr-poor vesuvianite crystal NRM #221142c, showing interfering absorption due to spin-forbidden Fe^{3+}-bands (vertical arrows) in the spectral range of the Cr^{3+} ν_2-band at ~23,000 cm^{-1}.

suggested by Manning (1968) for spectra of a Fe^{3+}-bearing vesuvianite from Lowell County, Vermont. The molar extinction coefficient of the field-independent absorption band at 21,600 cm^{-1}, which marks the $^6A_{1g}(S) \rightarrow {}^4A_1{}^4E(G)$ transition in ferric iron, was determined by Manning (1968) to be 1-2 $l \cdot mol^{-1} \cdot cm^{-1}$. This is in good agreement with the ε-value of 1.2 $l \cdot mol^{-1} \cdot cm^{-1}$ calculated from the O-spectrum of the least Cr-rich of the present crystals (#221142c). In addition to these bands, Manning (1968) recorded prominent spin-forbidden Fe^{3+}-bands at 23,100 and 16,500 cm^{-1}. These bands are poorly resolved in spectra of the present samples due to superposition with the much more intense spin-allowed Cr^{3+}-bands. The assymetry of the Cr^{3+} ν_2-band at ~23,000 cm^{-1} becomes more pronounced at decreasing Cr-content, which is related to a proportionally larger influence of the spin-forbidden Fe^{3+}-bands in this spectral region. This in turn is explained by the relatively high Fe^{3+}-contents, 1.33 -1.88 apfu, with the higher values found for the most Cr-poor of the present samples.
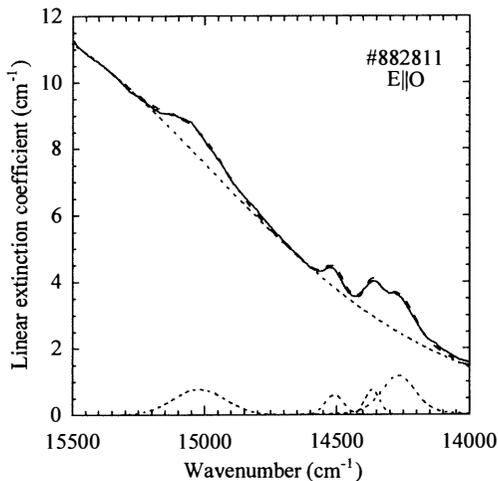
view of the comparable cation sizes for Cr^{3+} and Fe^{3+} in six-coordination, 0.615 and 0.645 Å (Shannon, 1976), and the absence of Jahn-Teller effects in both cations, it is reasonable to assume similar site occupancies for the two cations in the vesuvianite structure. As mentioned previously, the Mössbauer spectrum of one of the present samples shows a strong Fe^{3+} preference for the Y3-site and no evidence for Fe^{3+} occupancy at the Y2-site.

In the present spectra a number of additional less intense and narrow bands occur (fig. 7). These minor features display the characteristics of spin-forbidden d-d bands. They may be caused by electronic transitions in Cr^{3+} or Fe^{3+}. The intensity of the absorption bands located at approximately 26,000, 24,000, 21,600, and 19,300 cm^{-1} is not correlated with the Cr-content of the present samples and in fact the resolution of these bands improves considerably at decreasing Cr-content. As the present samples contain, apart from Cr, no other 3*d*-cations than ferric iron, it is reasonable to assign these weak bands to Fe^{3+} in the vesuvianite structure. The proposed assignment is in agreement with the one

Fig. 8 – Close-up of the E‖O-spectrum of sample NRM #882811, showing the spin-forbidden Cr^{3+}-bands superimposed on the low energy side of the spin-allowed Cr^{3+} ν_1-band at ~16,500 cm^{-1}. The bold solid line represents the measured spectrum and the dotted lines illustrate the computer resolved spectral features.

The relatively weak and sharp (FWHM= 60-230 cm^{-1}) absorption bands recorded in the present spectra at 14260, 14360, 14500 and 15020 cm^{-1} (fig. 8) display a positive intensity correlation with sample Cr-content. They mark spin-forbidden Cr^{3+} d-d transitions from the $^4A_{2g}$(F) ground state to energy levels derived from the ^2E_g(G) and $^2T_{1g}$(G) states. The observed band multiplicity is consistent with Cr^{3+} occupying a low-symmetry site.

The present spectra further reveal a sharp, weak and distinctly dichroic (E>O) absorption band at ~7,150 cm^{-1}, which is assigned to overtones of OH-stretching modes. In spectra of boron- and fluorine-free vesuvianite Groat *et al.* (1995) recorded two overlapping bands ascribed to overtones of OH-stretching modes at 7,170 and 7,130 cm^{-1}. These bands showed an identical polarisation (E>O) as in the present spectra. Notable is that the overtones of the OH-stretching modes decrease in energy with increasing F- and B-content (Groat *et al.*, 1995). Consequently, the observed high frequency of the OH-overtones in the present spectra further corroborates the results of the present EMP- and NRA-analyses.

Spectral intensity data and crystal fields parameters

From the results of the spectrum deconvolution (fig. 5 and Table 2) very good correlations between intensity and sample Cr-content are obtained. The linear regression coefficients (r^2-values) range from 0.958-0.994, with the lower r^2-values obtained for the v_2-band at ~23,000 cm^{-1}. The reason for this as well as the obtained positive regression values at Cr=0 is mainly due to a strong overlap between Fe^{3+} spin-forbidden bands and the Cr^{3+} spin-allowed absorption bands in the spectral region 21,000 - 25,000 cm^{-1}. Additional uncertainties are possibly related to the deconvolution of the low-energy wing of the UV absorption edge. For analytical purposes it is, in the case of Fe^{3+}-bearing vesuvianite, consequently more favourable to monitor Cr-contents through the intensity of

the v_1-band at ~16,500 cm^{-1}, where interferences are negligible. In this context it is worthwhile noting that the molar extinction coefficient of the v_1-band at ~16,500 cm^{-1} is relatively high (15 l·mol^{-1}·cm^{-1}) in E∥O and allows detection of Cr^{3+} at a concentration of ~0.25 wt.% Cr_2O_3 in a normal petrographic thin section (t=30 μm). Provided that vesuvianite crystals of larger sizes are available this detection limit can be improved. As the measured absorbance is directly proportional to sample thickness, a 300 μm thick vesuvianite sample would allow detection of Cr_2O_3-contents as low as 250 ppm. An advantage with Cr-detection from an O-spectrum is that for vesuvianite, being an optically uniaxial mineral, no pre-orientation of the analysed grain is necessary as all possible sections through the mineral will contain the O-direction in addition to an E´- or E-direction. Consequently, any vesuvianite grain in a thin section may be used for analytical application of spectral data.

The crystal field parameters obtained from the band analyses of the present spectra (Table 2) comprise a relatively low mean splitting parameter, 10Dq, of 16,500 (200) cm^{-1} and a moderate value of 667 (13) cm^{-1} for the Racah B-parameter. The value of 10Dq (or Δ) is directly obtained from the position of the v_1-band. The B-parameter, which may be regarded as a measure of the degree of bond covalency, is calculated from the equation B = $(2v_1$-$v_2)$ $(v_2$-$v_1)/(27v_1$-$15v_2)$. The resulting crystal field stabilisation energy (CFSE=12Dq) for Cr^{3+} at the Y(3)-site in vesuvianite is determined to 19,800 cm^{-1} (-236.9 kJ/g·ion). For coordination complexes with identical central ion and ligands, 10Dq is inversely proportional to the 5th power of the mean bond distance and consequently the splitting parameter is predicted to decrease rapidly with increasing bond length. In general there exists such a dependence between 10Dq and mean M-O bond distances for Cr^{3+}-bearing minerals (Burns, 1993). A detailed evaluation of the relationship is, however, not possible to perform at present as reported bond distances, obtained through XRD refinements, for most of

the spectroscopically studied minerals represent average values for sites mainly occupied by additional cations. Consequently, determined mean M-O distances do not reflect the actual Cr^{3+}-ligand distances, which are expected to deviate from such averaged values due to relaxation phenomena (Langer, 1999). However, as a comparison, similar 10Dq-values have been recorded for uvarovite and eskolaite, in which mean Cr^{3+}-ligand distances are 1,924 and 1,990 Å, respectively (Burns, 1993 and references therein). Averaged mean bond distances recorded for the Y(3)-site in vesuvianite are found to be in the same range, 1.94-1.97 Å (Groat *et al.*, 1992 and references therein). This indicates that negligble structural adjustments would be necessary for the incorporation of Cr^{3+} at the Y3-site of vesuvianite.

The calculated value of the Racah B-parameter of 667 cm^{-1} results in a nephelauxetic ratio β of 0.73 (relative to the free Cr^{3+}-ion value $B_\bullet$=918 cm^{-1} [Lever, 1984]). This is a distinctly higher value than found for Cr^{3+} in close-packed structures as spinel (B=617 cm^{-1}) but only slightly higher than the room temperature values retrieved (Taran *et al.*, 1994) for, e.g., Cr^{3+} at the Y-site in garnet group minerals (B=642-655 cm^{-1}). The observed higher B-value for Cr^{3+} in vesuvianite as compared to the garnet minerals indicates a larger reduction of the interelectronic repulsion at the vesuvianite Y3-site. A possible explanation for this is that only O^2-ligands surround the garnet Y-site, while the Y3-site in vesuvianite comprise O^2-ligands as well as OH$^-$-ligands, which induce less electron cloud expansion than oxygen ligands.

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