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ELECTRONIC SPECTROSCOPY EVIDENCE OF COMPENSATORY REPLACEMENT ${}^{\text{VI}}\text{Mg}{}^{\text{IV}}\text{Si} \rightarrow {}^{\text{VI}}(\text{Al}, \text{Cr}^{3+}){}^{\text{IV}}\text{Al}$ IN MANTLE ENSTATITES

Six samples of Cr-bearing enstatites with different contents of ${}^{\text{IV}}\text{Al}$ (0.012–0.127 apfu) and ${}^{\text{VI}}(\text{Al} + \text{Cr}^{3+})$ (0.019–0.130 apfu) from mantle xenoliths collected in kimberlitic pipes of Yakutia and South Africa were studied by electronic (optical) spectroscopy method. Calculated content of tetrahedral Al demonstrates perfect correlation ($R = 0.996$) with a sum of trivalent cations in octahedral positions, thus proving "orthohermakite" schema of heterovalent substitution ${}^{\text{VI}}(\text{Al}, \text{Cr}^{3+}) + {}^{\text{IV}}\text{Al} \rightarrow {}^{\text{VI}}\text{Mg}^{2+} + {}^{\text{IV}}\text{Si}$ in these samples. Two broad bands of spin-allowed electronic transitions of Cr^{3+} ions, ${}^4A_2 \rightarrow {}^4T_2$ (ν_1) and $\rightarrow {}^4T_1$ (ν_2), are present in all their polarized optical absorption spectra. Deconvolution of these spectra into separate Gauss components were carried out using *Peakfit 4.0* software (*Jandel Scientific*). Obtained results revealed splitting of Cr^{3+} -bands into components ν_{1a} , ν_{1b} , ν_{2a} and ν_{2b} , caused by transitions to levels ($E + A$) and ($E + A_1$) originated from split in trigonal crystal field excited states 4T_2 and 4T_1 , correspondingly.

It was determined that increase of ${}^{\text{IV}}\text{Al}$ and ${}^{\text{VI}}(\text{Al} + \text{Cr}^{3+})$ contents causes decrease of energies ν_{2a} and ν_{2b} , whereas ν_{1a} and ν_{1b} components show rising energies. This trend represents increase of crystal field parameter Dq due to shortening of interatomic distances in Cr^{3+} -bearing octahedra $M1$, and strong diminution of Rakah parameter B_{35} reflecting increasing covalence of Cr^{3+} –O chemical bond. The latter effect may be caused by rising effective charge of anions O^{2-} as a result of $\text{Al} \rightarrow \text{Si}$ substitution in tetrahedral positions that share ligands with $M1$ octahedra.

In general, the abovementioned effects are in a good agreement with changes in enstatite's crystal-chemical parameters, which follow "orthohermakite" schema of Me^{3+} substitution, as they were defined by X-ray studies. On the basis of the good correlation between ${}^{\text{IV}}\text{Al}$ and ${}^{\text{VI}}(\text{Al} + \text{Cr}^{3+})$, it was suggested that a local charge compensation as well as cluster formation (${}^{\text{VI}}\text{Cr}_1{}^{\text{IV}}\text{Al}_1$; ${}^{\text{VI}}\text{Al}_1{}^{\text{IV}}\text{Al}_1$ and their aggregations) take place in the structure of enstatites studied.

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Introduction. It is well known that electronic ("optical") spectroscopic parameters of Cr^{3+} ions are highly sensitive to crystal chemical peculiarities of Cr^{3+} -containing crystal matrix. There are many examples of successful employment of these spectroscopic data for the evaluation of chemical and structural features of Cr^{3+} -bearing minerals in mineralogical literature [1, 2, 9, 15, 17 etc]. Spectroscopic approach is especially useful in study of minerals from the mantle nodules in kimberlite pipes since chromium is typical element of deep-seated mineral associations.

Orthopyroxenes, enstatites ($\text{Mg}_2\text{Si}_2\text{O}_6$), belong to the main rock-forming minerals of many various magnesian types of mantle rocks and its chemical features — Al_2O_3 -contents particularly — are used by petrologists for evaluation of *PT*-con-

ditions of the respective mantle material [5, 6, 10, 12, 16, 18, 22 and others]. One of the important points of this question is the mechanism of charge compensation on the replacement of octahedral Mg^{2+} by Al^{3+} . For Al-containing enstatites, principally two compensatory schemes are possible: first $2{}^{\text{VI}}\text{Mg}^{2+} \rightarrow {}^{\text{VI}}\text{Al}^{3+} + {}^{\text{VI}}\text{Na}^{+}$ — the so-called "jadeite" scheme and second ${}^{\text{VI}}\text{Mg}^{2+} + {}^{\text{IV}}\text{Si}^{4+} \rightarrow {}^{\text{VI}}\text{Al}^{3+} + {}^{\text{IV}}\text{Al}^{3+}$ — the "orthohermakite" scheme. The first one is realized under high pressure conditions of diamond-pyrope facies [20], and the second is more characteristic for enstatites from the upper mantle and from crystal peridotites enriched by aluminium under conditions of moderate depth of the magmatic hearth. The latter scheme of the isomorphism of aluminium in enstatites was also confirmed by electronic spectroscopic study of the behaviour of Fe^{2+} – Fe^{3+} charge transfer bands in the absorption spectra [9]. Here, we report new results of an electronic

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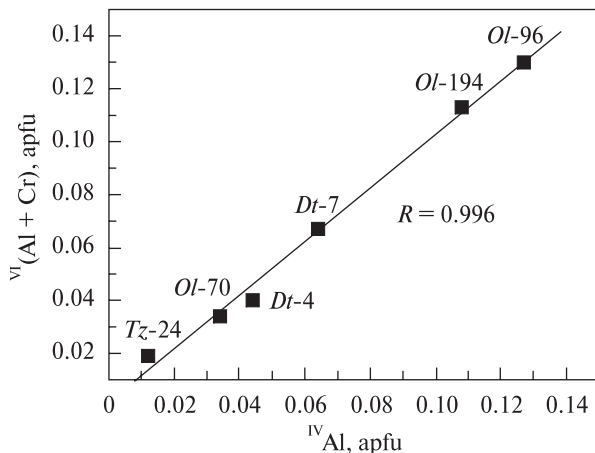


Fig. 1. Dependence of trivalent cations contents in octahedral sites of the enstatites studied on tetrahedral aluminum ^{IV}Al , apfu

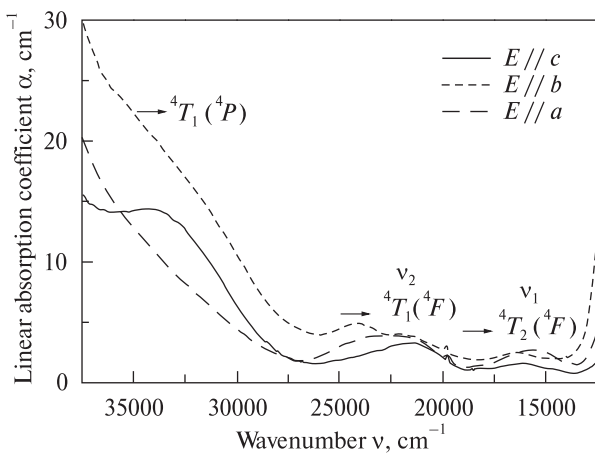


Fig. 2. Polarized electronic absorption spectrum of Cr^{3+} ions of enstatite *Tz-24* in the range 37500–12000 cm^{-1}

spectroscopic study of the Cr^{3+} -containing mantle enstatites with the purpose to evaluate the influence of the "orthoschermakite" replacing scheme on spectroscopic parameters of octahedral Cr^{3+} ions in this mineral.

Samples and Methods. Six chemically different, optically clear chromium-bearing enstatite crystals were separated from different mantle mineral associations (deep-seated xenoliths) in some kimberlite pipes of Yakutia and South Africa. In particular, the samples studied represent: *Ol-96* — spinel lherzolite, *Ol-194* — websterite, *Ol-70* — garnet lherzolite (all three are from "Obnazhonnaya" pipe, Yakutia), *Dt-4* and *Dt-7* — harzburgites from "Dyutouspen" pipe, South Africa, *Tz-24* — garnet harzburgite from "Udachnaya-western" pipe, Yakutia. All samples were studied by electronic absorption microspectroscopy. Their chemical

composition was analyzed by electron microprobe method in the same areas from which absorption spectra were obtained.

The examined enstatite crystals were divided each into two pieces, which were oriented by means of the spindelstage method and subsequently ground and polished to produce two plain-parallel slabs in planes (100) and (010), so that the spectra could be measured with $E // a'$ (*Y*), $E // b$ (*X*) and $E // c$ (*Z*) for every sample.

The spectra were scanned at room temperature using a microscope-spectrometer *ZEISS UMSP-80* (Technical University of Berlin, Germany) [13] in the spectral range 38000–12000 cm^{-1} with the measuring step 1 nm. Entrance and measuring apertures had diameters of 30 and 21 μm , respectively. The spectral slitwidth was 1 nm. The reference I_0 -spectrum was taken in air. Samples spectra were averaged from 20 scans. The single crystal polarized absorption spectra obtained were analyzed using the program *Peakfit 4.0* (*Jandel Scientific*).

Results and Discussion. Table 1 compiles the chemical compositions of the samples studied. It is obvious from the Table, that the chromium content in the samples varies in the range 0.009–0.037 apfu, whereas octahedral aluminum is in the range 0.003–0.107 apfu, tetrahedral aluminum — 0.009–0.127 apfu, and sodium — 0–0.010 apfu. The comparison of the $^{VI}(Al + Cr)^{3+}$, $^{VI}Na^+$ and ^{IV}Al contents indicate (with the exception of sample *Tz-24*) the "orthoschermakite" replacing scheme of R^{3+} -ions in octahedral sites of the enstatites studied here. Such a conclusion is confirmed by a high degree of positive correlation ($R = 0.996$) between the $^{VI}R^{3+}$ and ^{IV}Al contents,

Table 1. Chemical composition (atoms per formula unit) of the enstatites studied

Atom	<i>Tz-24</i>	<i>Ol-70</i>	<i>Dt-4</i>	<i>Dt-7</i>	<i>Ol-194</i>	<i>Ol-96</i>
Si	1.988	1.966	1.956	1.936	1.892	1.873
Ti	—	0.003	—	—	—	—
^{IV}Al	0.012	0.034	0.044	0.064	0.108	0.127
^{VI}Al	0.009	0.025	0.003	0.043	0.093	0.107
Cr	0.010	0.009	0.037	0.024	0.020	0.023
Fe	0.128	0.107	0.135	0.120	0.178	0.153
Mn	0.003	0.002	0.003	0.003	0.005	0.004
Mg	1.825	1.829	1.824	1.791	1.635	1.699
Ca	0.013	0.009	0.005	0.016	0.050	0.009
Na	0.009	0.003	0	0.007	0.005	0.004
Σ	3.997	3.987	4.007	4.004	3.986	3.999

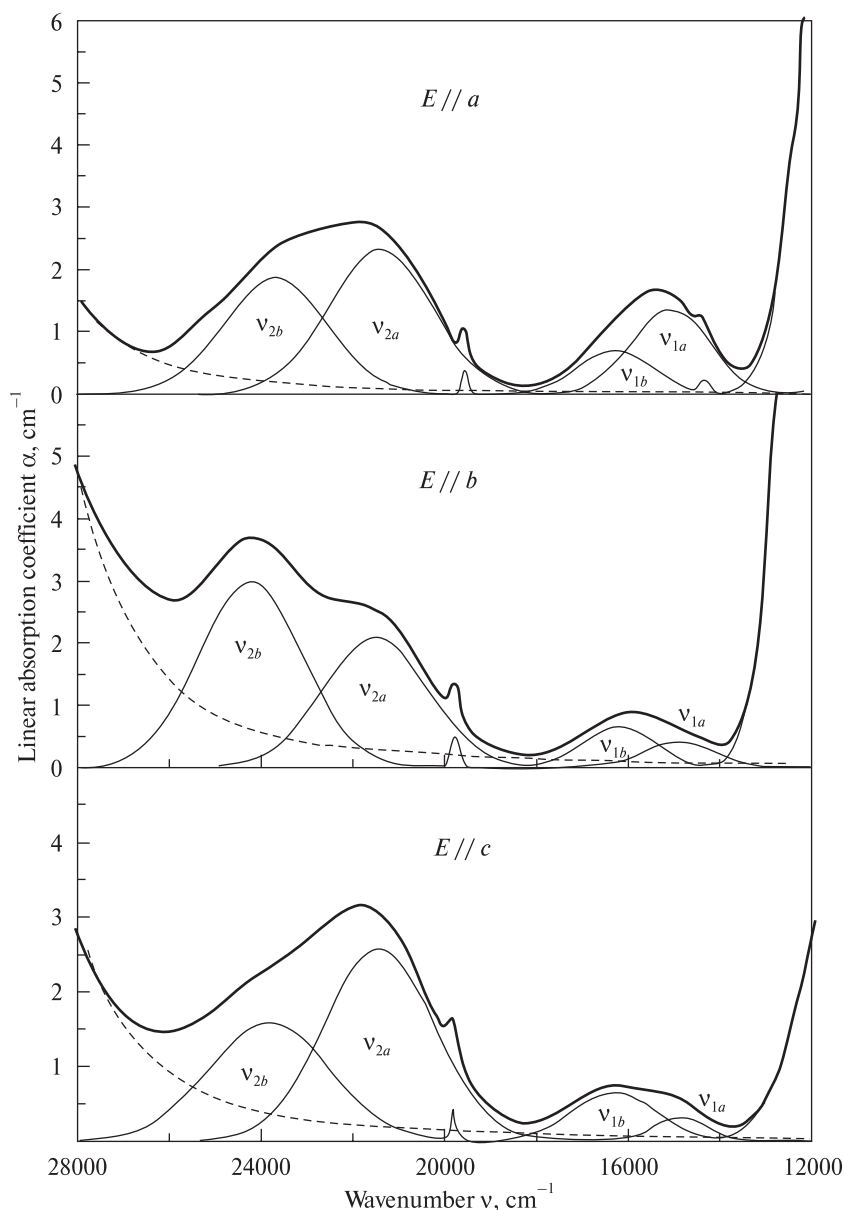


Fig. 3. An example of the resolution of the Cr^{3+} ions' polarized absorption spectra in enstatite $Tz-24$

which is graphically represented in Fig. 1. The deficiency of the charge balance in this case is a quantitative measure of a deviation from the "orthoschermakite" substitution and can be described by the following equation:

$${}^{\text{IV}}\text{Al}_{\text{apfu}} = 0.9815 \cdot {}^{\text{VI}}(\text{Cr}^{3+}, \text{Al})_{\text{apfu}} - 0.0011.$$

Single crystal polarized electronic absorption spectra in the range $35000\text{--}12000\text{ cm}^{-1}$ of the enstatite $Tz-24$ with the lowest tetrahedral aluminum content and, hence, lowest ${}^{\text{VI}}(\text{Al} + \text{Cr})_{\text{apfu}}$ among samples studied are shown in Fig. 2. In the visible region, the typical dd -bands of Cr^{3+} show up clearly. They are caused by the spin-allowed transitions ${}^4A_2(4F) \rightarrow {}^4T_2(4F)$ (ν_1) and ${}^4A_2(4F) \rightarrow {}^4T_1(4F)$ (ν_2). Besides these, a

distinct absorption band near 34000 cm^{-1} in the $E // c$ -spectrum is seen which is probably related to the ${}^4A_2(4F) \rightarrow {}^4T_1(4P)$ transition of Cr^{3+} in octahedral position.

All the other measurements of enstatites spectra were carried out in the spectral range $28000\text{--}12000\text{ cm}^{-1}$, to focus attention on correct resolution, i.e. fitting of the two absorption bands ν_1 and ν_2 of Cr^{3+} ions. An example of the deconvoluted into single bands spectra of $Tz-24$ enstatite is shown in Fig. 3. The spectroscopic parameters of the resolved absorption bands are represented in Table 2.

As one can see from Fig. 3, absorption bands ν_1 and ν_2 consist of two components each — ν_{1a} , ν_{1b} and ν_{2a} , ν_{2b} . This proves additional splitting of the

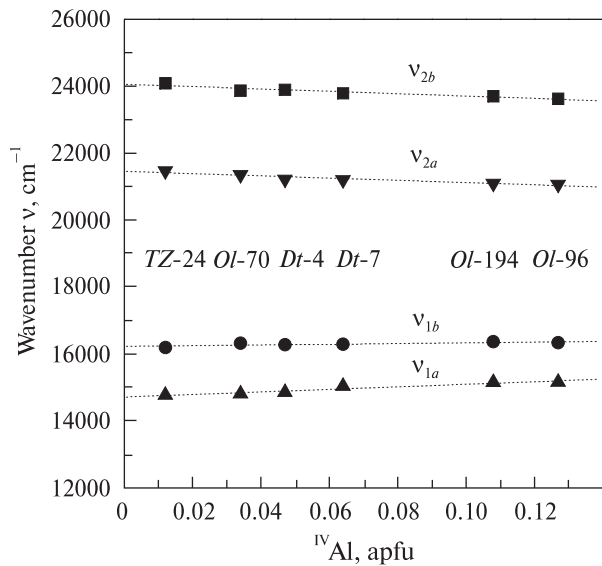


Fig. 4. Dependence of the Cr³⁺-absorption bands' energy in electronic spectra of the enstatites studied on tetrahedral aluminum contents

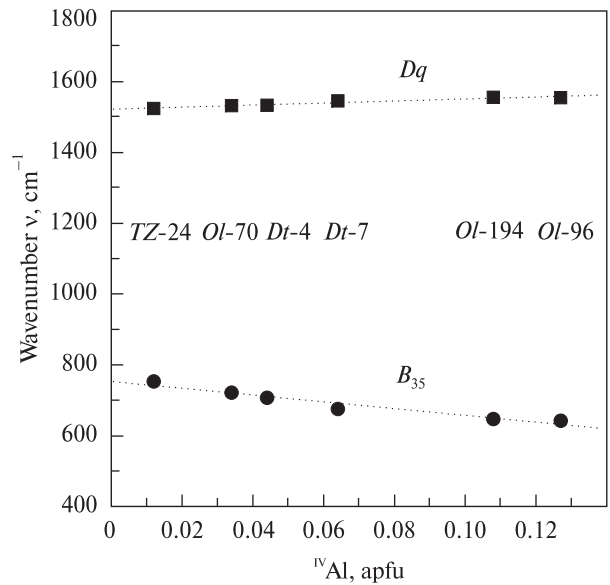


Fig. 5. Dependence of the crystal field parameter Dq and Racah parameter B_{35} on tetrahedral aluminum contents in the enstatites studied

excited electronic states, 4T_2 and 4T_1 , in the spectra of Cr³⁺ under the influence of the low-symmetry crystal field in the structure of the Cr³⁺-bearing enstatites.

The comparison of relative intensity of the most pronounced ν_{2a} and ν_{2b} bands in the polarized spectra leads to the following conclusion: the dd -electronic transition which determines the ν_{2b} band is allowed in the $E // b$ orientation, and the transition responsible for the ν_{2a} band is most intensive in the $E \perp b$ directions (parallel to crystallographic axes a and c). Taking into account the 4A_2 symmetry of the ground state, such selection rules for electronic transitions in Cr³⁺ ions can take a place when the symmetry of the split components of the excited Cr³⁺ levels is A_1 and E , respectively [14]. The same picture is observed for split components of 4T_2 level. Thus, the supposed scheme of the 4T_2 ($E + A$) and 4T_1 ($E + A_1$) splitting demonstrates an essential influence of a trigonal component on the

crystal field symmetry in Cr³⁺-centered octahedra. In our samples, the crystallographic axis b coincides with z -axis of the crystal field, a and c axes are close to CF axes x and y . The same orientations of the axes of dominant trigonal crystal field were reported earlier for Cr-bearing clinopyroxenes [8].

The spectroscopic parameters of the two components of the Cr³⁺-absorption bands ν_1 and ν_2 in the spectra of enstatites studied were averaged from the respective values of fitted single bands in the two opposed orientations $E // b$ and $E // c$, which reflect the spectral behaviour in the trigonal crystal field. An average energy value (in wavenumbers ν , cm⁻¹) for each absorption band were calculated in accordance with standard formulae for electronic spectra of Cr³⁺ ions in trigonal field: $\nu_{2a} = 1/3[2\nu_{2a}(E // c) + \nu_{2a}(E // b)]$. The values of $\nu_1 = 10Dq$ (the 4T_2 -level position over the ground state) and ν_2 (the 4T_1 -level position over the ground state) yielded the crystal field para-

Table 2. Parameters of absorption bands caused by Cr³⁺ ions in polarized optical spectra of enstatite *Tz-24*: energy ν , full width on half height $\Delta\nu_{1/2}$ and intensity α , cm⁻¹

Band	$E // a'$			$E // b$			$E // c$		
	ν	$\Delta\nu_{1/2}$	α	ν	$\Delta\nu_{1/2}$	α	ν	$\Delta\nu_{1/2}$	α
ν_{1a}	15 180	2040	1.36	14 770	1450	0,38	14 850	1150	0.31
ν_{1b}	16 330	1950	0.76	16 200	1620	0.67	16 230	2060	0.65
ν_{2a}	21 600	2740	2.32	21 520	2570	2.02	21 570	2950	2.57
ν_{2b}	24 060	2750	1.88	24 150	2630	2.91	24 070	2810	1.58

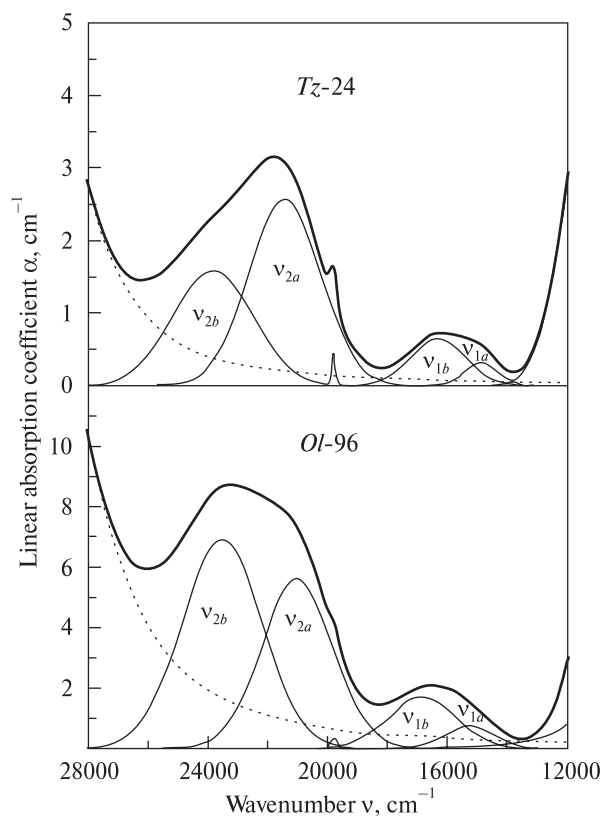


Fig. 6. Comparative intensities of the ν_{2a} and ν_{2b} absorption bands in the $E//c$ -polarized electronic spectra of enstatites with lowest (*Tz-24*) and highest (*Ol-96*) amount of tetrahedral aluminum

meter Dq and were used to calculate the values of the Racah parameter B_{35} , which reflects the degree of covalency of the $\text{Cr}^{3+}\text{-O}$ bonds.

As it follows from the results of these calculations, shown in Table 3 and in Figs 4 and 5, the increase of $^{\text{IV}}\text{Al}$ contents in the enstatites studied results in appreciable change of spectroscopic characteristics of Cr^{3+} -absorption bands and, in a consequence, it causes changes of crystal field parameters Dq and B_{35} of Cr^{3+} -containing octahedral sites. The most remarkable changes appear

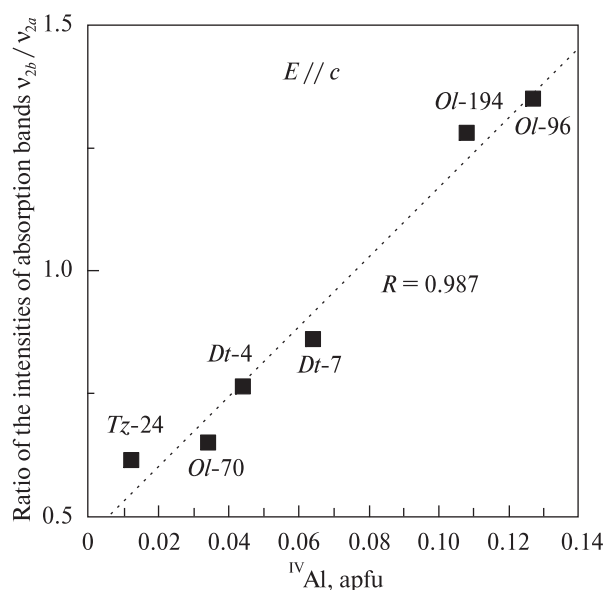


Fig. 7. Dependence of the intensities' ratio of Cr^{3+} -absorption bands ν_{2b} and ν_{2a} in the $E//c$ -polarized electronic spectra on tetrahedral aluminum contents in the enstatites studied

as decrease in energy of bands ν_{2a} , ν_{2b} and simultaneous increase of ν_{1a} and ν_{1b} energy. This increase of the 4A_2 (4F) \rightarrow 4T_2 transition energy (absorption band ν_1) proves the increase of the Dq value in accordance with the well known equation $10Dq = 1/R^5$, derived from crystal field theory [4]. This effect reflects decrease of the $\text{Cr}^{3+}\text{-O}$ interatomic distances, i. e. decrease of the size of the Cr^{3+} -containing octahedral sites next to Al-tetrahedra. The decrease of the energy gap between 4T_2 and 4T_1 levels results in essential decrease of the Racah parameter B_{35} . This observation can be interpreted in terms of increasing covalency of the $\text{Cr}^{3+}\text{-O}$ bonds (Table 3).

Increasing $^{\text{IV}}\text{Al}$ contents exert a great influence also on relative intensity I (α , cm^{-1}) of the Cr^{3+} -absorption bands. Such an effect is displayed most clearly if we compare the ν_2 components in

Table 3. Spectroscopic parameters of Cr^{3+} ions in the mantle enstatites studied

Sample	$^{\text{VI}}\text{Cr}^{3+}$	$^{\text{IV}}\text{Al}$	Spectroscopic parameters, cm^{-1}					
			apfu				Dq	B_{35}
			$\rightarrow {}^4E$ (4T_2)	$\rightarrow {}^4A_1$ (4T_2)	$\rightarrow {}^4E$ (4T_1)	$\rightarrow {}^4A_2$ (4T_1)		
<i>Tz-24</i>	0.010	0.012	14770	16200	21470	24090	1524	753
<i>Ol-70</i>	0.009	0.034	14810	16330	21360	23870	1532	721
<i>Dt-4</i>	0.037	0.044	14850	16280	21220	23890	1533	704
<i>Dt-7</i>	0.024	0.064	15040	16290	21200	23790	1546	675
<i>Ol-194</i>	0.020	0.108	15150	16370	21100	23700	1556	647
<i>Ol-96</i>	0.023	0.127	15160	16340	21070	23630	1555	642

$E // c$ -spectra of the enstatites with lowest ($Tz-24$) and with highest ($Ol-96$) ^{IV}Al contents (Fig. 6). Fig. 7 shows the ratio I_{v2b}/I_{v2a} for spectra of all samples studied as a function of the ^{IV}Al contents. The strong correlation ($R = 0.987$) between these parameters proves again the first remark of this paragraph.

It is necessary to refer to results of the X -ray investigations of a structure of Al-bearing orthopyroxenes for the crystal-chemical interpretation of the revealed dependencies. According to numerous data on structural refinements of natural and synthetic enstatites with the orthoschermakite admixture [3, 5, 11, 19, 21], tetrahedral aluminum is almost completely ordered in SiB sites having common oxygen atoms ($O1B$, $O1B'$ and $O2B$) with $M1$ -octahedral sites containing the trivalent atoms Al and Cr. Such an arrangement of neighboring Al-tetrahedra and $M1$ octahedra results in decreasing of the $M - OB$ interatomic distances and degree of the $M1$ -octahedra distortion [5].

As one can see, the data presented above about the character of the ^{IV}Al influence on spectroscopic parameters of Cr^{3+} ions in enstatites are in agreement with conclusions of structural studies based on X -ray results. Note first increase of the $Dq_{Cr^{3+}}$ values with increasing of the ^{IV}Al contents that undoubtedly confirms the decreasing of $M1$ size. The rise of the $Cr^{3+}-O$ bond covalency in ^{IV}Al -enriched enstatites is caused obviously by decreasing covalency in adjacent tetrahedral sites, i.e. when $Si \leftarrow Al$ replacement proceeds. Finally, changing of the local symmetry of the $M1$ -sites, and consequently changing of selection rules may cause the observed change of the adsorption bands' relative intensity with increasing ^{IV}Al contents.

The distinct dependence between $^{VI}(Cr + Al)^{3+}$ and $^{IV}Al^{3+}$ contents ($R = 0.996$) proves local charge compensation, that is formation of clusters

$^{VI}Cr_1^{3+}{}^{IV}Al_1$ or more complicated aggregations like $^{VI}Cr_n^{3+}{}^{IV}Al_m$. In the structure of orthopyroxenes studied here, the ^{IV}Al ions as second-sphere cations share common ligands with octahedral Cr^{3+} ions and, naturally, have definite influence on spectroscopic characteristics of the latter.

It is obvious that the model of the local charge compensation discussed above assumes formation of $^{VI}Al_1{}^{IV}Al_1$ clusters as well as more complicated aggregates in the enstatite structure. Such types of clusters, even in case of their statistical distribution, should also influence the spectroscopic characteristics of Cr^{3+} ions in $M1$ sites (see above). According to data reported by Ganguly and Ghose [5], total contents $^{VI}Al + ^{IV}Al = 0.26$ apfu in synthetic aluminous orthopyroxene causes appreciable changing in the geometry of $M1$ and especially $M2$ sites. In particular, it leads to a decrease of the ($M1$, $M2$) — O interatomic distances. Since $^{VI}Al_1{}^{IV}Al_1$ clusters, as well as chromium-bearing clusters $^{VI}Cr_1^{3+}{}^{IV}Al_1$, are partly incorporated into the same chains of edge-sharing $M1$ octahedra, each of the clusters has common edges with three $M2$ -octahedra [7]. Thus Al-clusters have influence on sizes and local symmetry of all sites in octahedral chains including the Cr^{3+} -centered $M1$ sites.

From the discussed above spectroscopic data we can conclude that the influence of the "orthoschermakite" replacement on the spectroscopic parameters of Cr^{3+} ions, i. e. on the energy of absorption bands, crystal field parameter Dq and degree of the covalency of the $Cr^{3+}-O$ bond B_{35} in mantle enstatites is caused by the influences of $^{VI}Cr_1^{3+}{}^{IV}Al_1$ and $^{VI}Al_1{}^{IV}Al_1$ clusters or their aggregates. It is quite clear that such an effect is mostly displayed in samples with the largest ^{IV}Al contents as, for instant, in enstatite $Ol-96$, where total Al contents reaches 0.234 apfu.

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РЕЗЮМЕ. Шість зразків Cr³⁺-вмісних енстатитів з різним вмістом ^{IV}Al (0,012—0,127 а. ф. о.) і ^{VI}(Al + Cr³⁺) (0,019—0,130 а. ф. о.) із ксенолітів мантійних порід в кимберлітових трубках Якутії і Пд. Африки вивчені за допомогою методу оптичної (електронної) спектроскопії. Вмісти тетраедричного алюмінію і тривалентних катіонів у октаедричних позиціях структури вивчених зразків енстатитів зв'язані коефіцієнтом кореляції $R = 0,996$, що однозначно свідчить про "орточермакітову" схему гетеровалентного ізоморфного заміщення іонів Mg²⁺ домішковими атомами (Al + Cr)³⁺. У поляризованих спектрах оптичного поглинання фіксуються дві широкі складні смуги іонів Cr³⁺, викликані спін-дозволенними електронними переходами ${}^4A_2 \rightarrow {}^4T_2 (v_1)$ і $\rightarrow {}^4T_1 (v_2)$. Виконане для всіх поляризацій ($E // a'$, $E // b$ та $E // c$) розкладання смуг, що спостерігаються, на елементарні (гауссові) функції з використанням програми *Peakfit 4.0 (Jandel Scientific)* виявило розщеплення цих смуг на компоненти v_{1a} , v_{1b} , v_{2a} й v_{2b} , пов'язані з переходами на розщеплені тригональним кристалічним полем рівні збуджених станів ${}^4T_2 (E + A)$ і ${}^4T_1 (E + A_1)$.

Встановлено, що зі збільшенням вмісту ^{IV}Al та ^{VI}(Al + Cr³⁺) у вивчених енстатитах значення енергії смуг поглинання v_{2a} та v_{2b} зменшуються, а смуг v_{1a} та v_{1b} — збільшуються, що призводить до збільшення параметра кристалічного поля Dq , що свідчить про зменшення розмірів Cr³⁺-вмісних октаедричних позицій $M1$, а також до істотного зменшення значення параметра Ракá B_{35} (тобто до підвищення ступеня ковалентності зв'язку Cr³⁺—O). Останній ефект обумовлений, скоріш за все, збільшенням ефективного заряду іонів кисню під час заміщення кремнію алюмінієм в SiB-тетраедрах, що мають спільні ліганди з $M1$ -позиціями.

У цілому відзначені вище ефекти цілком узгоджуються із встановленим рентгеноструктурним методом характером зміни кристалохімічних параметрів енстатитів за "орточермакітову" схеми входження тривалентних домішок в ортопіроксенову структуру. На підставі високого ступеня кореляції значень вмісту тетраедричного алюмінію й тривалентних катіонів висловлене припущення про локальний механізм компенсації заряду з утворенням кластерів типу ^{VI}Cr₁³⁺ ^{IV}Al₁ та ^{VI}Al₁ ^{IV}Al₁ або більш складних їх агрегацій у структурі вивчених енстатитів.

РЕЗЮМЕ. Шість образцов Cr³⁺-содержащих энстатитов с разным содержанием ^{IV}Al (0,012—0,127 а. ф. е.) и ^{VI}(Al + Cr³⁺) (0,019—0,130 а. ф. е.) из ксенолитов мантийных пород в кимберлитовых трубках Якутии и Ю. Африки изучены с помощью метода оптической (электронной) спектроскопии. Содержания тетраэдри-

ческого алюминия и трехвалентных катионов в октаэдрических позициях структуры изученных образцов энстатитов связаны коэффициентом корреляции $R = 0,996$, что однозначно свидетельствует об "орточермакитовой" схеме гетеровалентного изоморфного замещения ионов Mg^{2+} примесными атомами $(Al + Cr)^{3+}$. В поляризованных спектрах оптического поглощения фиксируются две широкие сложные полосы поглощения ионов Cr^{3+} , вызванные спин-разрешенными электронными переходами ${}^4A_2 \rightarrow {}^4T_2 (v_1)$ и $\rightarrow {}^4T_1 (v_2)$. Выполненное для всех поляризаций ($E//a'$, $E//b$ и $E//c$) разложение наблюдаемых полос на элементарные (гауссовы) функции с использованием программы *Peakfit 4.0 (Jandel Scientific)* выявило расщепление этих полос на компоненты v_{1a} , v_{1b} , v_{2a} и v_{2b} , связанные с переходами на расщепленные тригональным кристаллическим полем уровни возбужденных состояний ${}^4T_2 (E + A)$ и ${}^4T_1 (E + A_1)$.

Установлено, что с увеличением содержания ${}^{IV}Al$ и ${}^{VI}(Al + Cr^{3+})$ в изученных энстатитах значения энергии полос поглощения v_{2a} и v_{2b} уменьшаются, а полос v_{1a} и v_{1b} — увеличиваются, что приводит к увеличению параметра кристаллического поля Dq , что свидетельствует об уменьшении размеров Cr^{3+} -содержащих октаэдрических позиций $M1$, и существенному уменьшению значения параметра Рака B_{35} (повышению степени ковалентности связи $Cr^{3+}-O$). Последний эффект обусловлен, очевидно, увеличением эффективного заряда ионов кислорода при замещении кремния алюминием в SiB -тетраэдрах, имеющих общие лиганды с $M1$ -позициями.

В целом отмеченные выше эффекты полностью согласуются с установленным рентгеноструктурным методом характером изменения кристаллохимических параметров энстатитов при "орточермакитовой" схеме вхождения трехвалентных примесей в ортопироксеновую структуру. На основании высокой степени корреляции значений содержания тетраэдрического алюминия и трехвалентных катионов высказано предположение о локальном механизме компенсации заряда и образовании кластеров типа ${}^{VI}Cr_1^{3+} {}^{IV}Al_1$ и ${}^{VI}Al_1 {}^{IV}Al_1$ или более сложных их агрегаций в структуре изученных энстатитов.