Cr³⁺ in phyllosilicates: Influence of the nature of coordinating ligands and their next cationic neighbors on the crystal field parameters

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Abstract—The electronic absorption spectra of Cr^{3+}-bearing clinochlore (I, kämmererite), amesite (II), muscovite (III, fuchsite), dickite (IV), and montmorillonite (V, volkonskite) analysed by electron microprobe were obtained on single crystals. Microscope-spectrometric techniques and polarized radiation in the spectral range 10000-38000 cm^{-1} (I, II, III) or (on fine grained material) diffuse reflectance spectrometry in the spectral range 8000-50000 cm^{-1} (IV, V) were used. The ligand field theoretical evaluation of the spectra showed the following: (i) The $\Delta_o = 10Dq = f(1/R^5)$ relation, wherein Δ_o is the octahedral crystal field parameter and R the mean cation ligand distance, is valid within each series of layer silicates containing octahedral Cr^{3+} either in a trioctahedral layer (I, II and phlogopite) or in a dioctahedral layer (III, IV, V). Between the two functions, $\Delta_{o,trioct} = f(1/R^5_{trioct})$ and $\Delta_{o,dioct} = f(1/R^5_{dioct})$, there exists an energy difference of about 2200 cm^{-1}. (ii) There is no support for the sequence of the effective charges of $OH^- < O^{2-}$ as suggested by the spectrochemical series. Quite the contrary, Δ_o decreases in the sequence $Cr(OH)_6$ (I), $CrO_2(OH)_4$ (II), $CrO_4(OH)_2$ (phlogopite). (iii) A negative higher-order correlation between Racah parameter B and crystal field parameter Δ_o exists, indicating an increase in covalency of the Cr-(O,OH) bond with increasing strength of the crystal field, wherein the dioctahedral t-o-t phases represent lowest Δ_o and highest B. This is interpreted to result from next-neighbor effects on the $(Si_{1-x}Al_x)$-coordinated apical oxygens forming, together with 2 OH^-, the octahedral coordination in the o-layers of these phases.

INTRODUCTION

THE LIGAND FIELD theoretical evaluation of electronic absorption spectra of $3d^N$ transition metal ion-bearing, oxygen based minerals (*e.g.*, LEVER, 1984; SCHLÄFER and GLIEMANN, 1980) reveals the octahedral crystal field parameter $\Delta_o = 10Dq$, possibly parameters describing the distortion of the field from cubic symmetry (KÖNIG and KREMER, 1977), and the Racah parameters B and C, taking into account the interelectronic repulsion of the d-electrons (TANABE and SUGANO, 1954a,b).

The octahedral crystal field parameter $\Delta_o = 10Dq$, which allows for the calculation of the crystal field stabilization energy of the respective $3d^N$-ion in the respective structural site or sites (*e.g.*, BURNS, 1970, 1993), is theoretically derived from the point charge model of the crystal field theory as

$$10_{Dq} = \frac{5}{3} \frac{Z_L \times e^2}{R^5} \langle r^4 \rangle \qquad (1)$$

(*e.g.*, DUNN *et al.*, 1965; LEVER, 1968). Herein, Z_L is the effective charge of the ligands, R is the mean central ion-ligand distance and $\langle r^4 \rangle$, the mean value of the forth power of the radial distance of the 3d-orbitals from the nucleus.

Equation 1 is appropriate to determine, from spectroscopically measured 10Dq-values, mean distances between central $3d^N$-ion and its ligands in various oxygen-based mineral structures. Such distances are local values, which are valid for the $3d^N$-ion containing site or, in the case of substitutive Cr^{3+}, of that part of the respective crystallographic site where the substitution inside the structure really occurs. This procedure presupposes that the same transition metal ion is considered and that the product $(Z_L \cdot e^2) \cdot \langle r^4 \rangle$ is constant. The latter assumption is, at least in a first approximation, fulfilled for $3d^N$-ion containing solid solutions, *i.e.* in one and the same structural type. Indeed, it has been shown that mean local octahedral $3d^N$-oxygen distances can be obtained from spectra of intermediate members of solid solution series (LANGER, 1988).

On the other hand, the above approach is likely to fail when comparing different structure types, because the product $(Z_L \cdot e^2) \cdot \langle r^4 \rangle$ is not constant. This is indicated by observations on the Racah B vs. Cr—O distances of various minerals (ABU-EID and BURNS, 1976) as well as by a study of some chromium-bearing minerals from altered rocks by EXAFS and electronic spectroscopy (CALAS *et al.*, 1984). Recently, the influence of next nearest cations on the effective charge of the ligands, *i.e.* on $Z_L \cdot e^2$, was qualitatively demonstrated for the

case of chromium-bearing amesite (PLATONOV *et al.*, 1995).

It is the aim of the present paper to study the influence of changing effective charge of the ligands on the crystal field parameters and the degree of covalency of the ligand-central ion bonds. For this purpose we obtained and evaluated the electronic absorption spectra of a series of Cr^{3+}-bearing sheet silicates with structures that are especially appropriate for the following reasons:

(i) The phyllosilicates, whether they are of the 2:1-(T—O—T)-type or of the 1:1-(T—O)-type, provide octahedral layers isolated from each other and interconnected with T-layers only. This allows for the study of influences of the cationic neighbours of the second coordination sphere on the coordinating ligands of an octahedron under consideration.

(ii) The coordination octahedra within the O-layers of different phyllosicates provide $[O_{6-n}(OH)_n]$ ligands where n_{OH} may be 2 in 2:1-minerals, 4 in 1:1-minerals, and 6 in the interlayer sheets of chlorites.

(iii) The site occupancies in the O-layers may be different. Thus there exist a variety of different next neighbor relations for the ligands of an octahedron under consideration.

SAMPLES AND METHODS

The following samples were studied:
(1) *Chromian clinochlore (kämmererite)*, mm-sized, clear and inclusion-free single crystals approximately 100 μm thick, from the Erzincan deposit, Turkey (BAILEY, 1986) with perfect cleavage parallel (001) and weak pleochroism in purple hues.
(2) *Chromian amesite:* Small, clear, lilac crystals from Sobótka deposit, Poland (PLATONOV *et al.*, 1995).
(3) *Chromian muscovite (fuchsite)*, clear, emerald green, platy crystals, similar in size and thickness as the kämmererite sample, from Murun-keu eclogites, Arctic Urals, Russia (UDOVKINA, 1971).
(4) *Chromian dickite,* fine-grained aggregate of semitransparent quartz crystallites and powdery bluish-green dickite in 3.5:1 proportion (pseudo-jade) from Chinlon deposit, China (CAO YUNGCHENG, 1983).
(5) *Volkonskoite (chromium montmorillonite)*, deep-green, fine-grained aggregate from Urals, Russia (YUSHKIN *et al.*, 1986).

Microprobe analyses

Microprobe data are presented in Table 1. They were obtained on the Camebax Microbeam in the ZELMI-laboratory at the Technical University of Berlin using the following standards: natural quartz (Si), wollastonite (Ca), rutile (Ti), spinel (Al), olivine or spinel (Mg), albite (Na) and metallic iron or chromium (Fe or Cr). The microprobe beam diameter was 2 μm with acceleration voltage of 15 kV and beam current of 20 nA. The chromium-bearing pseudo-jade was analyzed by OES-ICP. Because this material is not single phase, the data obtained are not included in Table 1. Its essential feature for the present purpose is the chromium content, which is calculated to be near 0.09 wt% Cr from the analytical data and the quartz to dickite proportion (see above).

Preparation of samples and spectroscopic measurements

Where grain sizes were large enough, *i.e.* in case of clinochlore, amesite and muscovite, individual crystals could be oriented and prepared for polarized single crystal spectroscopy. In these cases, the crystals were oriented by means of spindle stage methods, embedded in the oriented position and subsequently ground and polished on two opposite sides to produce slabs on which up to two polarizations could be measured. Slabs parallel to (001) were prepared for all three minerals mentioned and additional slabs parallel to (001) were prepared in case of clinochlore and muscovite. Hence, for the two latter minerals spectra with E∥X (α-spectra), E∥Y (β-spectra) and E∥Z (γ-spectra) could be recorded. In case of amesite, only spectra parallel and perpendicular to the c-axis were obtained.

The single crystal spectra in the spectral range 38000 to 12000 cm^{-1} were scanned at room temperature in a microscope-spectrometer (Zeiss UMSP-80) using UV-transparent optics (Zeiss Ultrafluars 10×) and a Glan-Thompson-type calcite prism polarizer. Entrance and measuring apertures had effective diameters of 30 and 21 μm, respectively. The spectral slit width was 1 nm and the step width was also 1 nm. The reference I_o-spectrum was taken in air. Sample spectra were averaged from 20 scans.

In the case of dickite and volkonskoite, where no single crystal spectra could be obtained, powder reflectance spectra were scanned in the range 50000 to 10000 cm^{-1} using a Perkin-Elmer Lambda 19 spectrometer equipped with an integrating sphere covered with teflon as the reflecting material. The compact natural sample was ground and polished on one side before measurement. Teflon powder served as a white standard. Measuring steps were 0.1 nm, the spectral resolution was between 0.05 an 5 nm and the wavelength accuracy was 0.15 and 0.6 nm in the UV/VIS and NIR, respectively.

Evaluation of the spectra

The band characteristics in the polarized single crystal spectra, especially the position of the band maxima, were obtained by applying peak fitting procedures (program PeakFit, Jandel Scientific, 1991) assuming a Gaussian shape for the component bands. The energy values for the band maxima of the various polarization directions were averaged. The accuracy of the average values obtained is better than 50 cm^{-1}. Energy positions of band maxima in powder reflectance spectra were obtained by the same fitting procedures, resulting in the accuracy of band positions mentioned above.

RESULTS AND DISCUSSION

The crystal chemistry of the minerals under study (Table 1) is typically characterized by their chromium content, while other substituting transition elements are low in concentration. The polar-

Table 1. Composition of chromian phyllosilicates studied as obtained by electronmicroprobe analyses given in wt% of the oxide components and in atoms per formula units. n.d. = below the limit of detection. t = tetrahedral layer, o = octahedral layer, i.l. interlayer

Oxide components [wt.%]	Clinochlore (kämmererite)	Amesite	Muscovite (fuchsite)	Montmorillonite (volkonskoite)
SiO$_2$	33.81	21.70	49.49	47.09
TiO$_2$	n.d.	n.d.	0.89	n.d.
Al$_2$O$_3$	8.08	32.15	30.10	3.10
Fe$_2$O$_3$ tot.	1.37	0.46	1.18	0.97
Cr$_2$O$_3$	7.47	3.37	0.55	21.05
MgO	35.02	27.03	3.31	8.55
CaO	n.d.	n.d.	n.d.	4.21
Na$_2$O	n.d.	n.d.	0.85	n.d.
K$_2$O	n.d.	n.d.	10.06	0.19
Total	85.60	84.67	96.27	85.05
Basis	28 neg. charges	14 neg. charges	22 neg. charges	22 neg. charges
Si	3.29 } 4.00^t	1.05 } 2.00^t	3.26 } 4.00^t	4.04^t
Al$^{[4]}$	0.71	0.95	0.74	
Mg$^{[6]}$	3.00°			
Al$^{[6]}$	0.21	0.88	1.60	0.31
Ti	<0.01	<0.01	0.04	<0.01
Fe^{3+}	0.12 } 2.99$^{i.l.}$	0.02 } 2.98°	0.06 } 2.06°	0.07 } 2.67°
Cr^{3+}	0.58	0.13	0.03	1.43
Mg	2.08	1.95	0.33	0.86
Ca	<0.01	<0.01	<0.01	0.39
Na	<0.01	<0.01	0.11 } 0.95$^{i.l.}$	<0.01 } 0.60$^{i.l.}$
K	<0.01	<0.01	0.84	0.21

ized electronic absorption spectra of Fig. 1 as well as the unpolarized spectra in Fig. 2 show the two strong bands, v_1 and v_2, in the visible range. They are typical of dd-transitions of octahedral Cr^{3+} and are derived from the transitions $^4A_{2g}$-$^4T_{2g}$ (F) and $^4A_{2g}$-$^4T_{1g}$ (F), respectively, under point symmetry O$_h$. The unpolarized reflectance spectra of Fig. 2 show an additional broad band in the UV, attached to the UV-absorption edge. This band is displayed in the polarized spectra of amesite only. The reason is that the UV above about 33000 cm^{-1} is masked in the other spectra by absorption in the embedding epoxy resin. A peculiarity of the muscovite spectra is the position of the UV edge at relatively low energies compared to the spectra of the other minerals. This may be due to the Fe^{3+} content of this sample (Table 1).

The polarization of the two bands, v_1 and v_2, displayed in Fig. 1 is caused by symmetry related selection rules of the respective transitions of Cr^{3+} in the octahedra of low site symmetry in the structures of the minerals under study. Because a true low-symmetry ligand-field treatment is currently possible only in special sases (KÖNIG and KREMER, 1977; cf. also WILDNER and LANGER, 1994) and

because the actual or effective octahedral site symmetries in the mineral structures involved here are lower than orthorhombic, our interpretation is based on the commonly used approximation of the cubic crystal field parameter Δ_o = 10Dq. In this procedure, the averages of band maxima in the different polarizations are determined (see above). Crystal field parameters obtained by this approximation are slightly lower than the correct ones (1.3% in corundum, cf. LANGER and ANDRUT, 1996). This will not influence the conclusions to be drawn in this paper, as the slight error introduced is expected to be nearly the same in all the phases studied here. However, for these reasons, the band polarizations observed in Fig. 1 will not be evaluated in detail.

The values obtained are listed in Table 2, along with the relevant crystallochemical characteristics. The band positions listed are used to calculate the parameters quoted in the right part of the table, which characterize octahedral Cr^{3+} in the respective structural matrix. The cubic crystal field parameter Dq is equal to $^1/_{10}$ of the energy of v_1. The Racah parameter B is derived from v_1 and v_2 using the respective solutions of the secular determinant
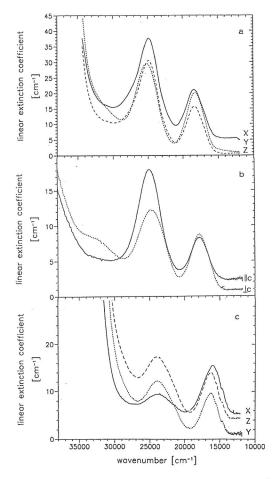
FIG. 1. Electronic single crystal absorption spectra of chromium-bearing clinochlore (a), amesite (b) and muscovite (c). The orientation of the electrical vector of the measuring radiation is given at the respective absorption spectrum. Measurements are performed at ambient conditions. For compositions of samples see Table 1.

(cf., e.g., LEVER, 1984). The quantity of B, taking into account the interelectronic repulsion of the d-electrons of Cr^{3+}, is a measure of the degree of covalency of the chromium-oxygen bond. To characterize differences in covalency, it is general practice to calculate the nephelauxetic ratio $\beta = B_{ion,cryst}/B_{ion,free}$. The free ion value, $B_{ion,free}$, for Cr^{3+} adopted here is 918 cm^{-1} (TANABE and SUGANO, 1954a). Finally, the table compiles the crystal field stabilization energy of Cr^{3+} in octahedral coordination in the minerals listed.

Using the values of the crystal field parameters Dq and B quoted in Table 2, it is possible to calculate the energy of a third spin-allowed transition of octahedral Cr^{3+}, $^4A_{2g}-^4T_{1g}$ (P), which is expected

in the UV and possibly causes the aforementioned broad band in this spectral region. The calculation is done by using the respective solution of the secular determinant for the excited state (cf., eg., LEVER, 1984). The band positions as observed in the spectra of amesite (32400 cm^{-1}) of dickite (37300 cm^{-1}) and of volkonskoite (38300 cm^{-1}) compare well with the values calculated for the above transitions to the excited crystal field state derived from ^4P, which are 33900, 37200 and 36200 cm^{-1}, respectively. The fair agreement between calculated and observed values indicates that the above assignment is correct. It might be mentioned here that this transition has been to date observed in only a few chromium-bearing minerals.

The octahedral first coordination sphere of the central Cr^{3+}-ions is different in three aspects in the structures of the various minerals studied: (i) the mean Cr^{3+}-(O,OH) distances, R, in the structures, (ii) the ratio of oxygen and hydroxyl per octahedron, (iii) the next neighbor situation of the ligands as created by the dioctahedral or trioctahedral nature and the cationic population of the octahedral sites by cations other than Cr^{3+}.
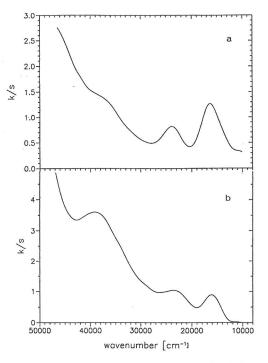

FIG. 2. Electronic absorption spectra, scanned as diffuse reflectance spectra, of chromium-bearing dickite (a) and volkonskoite (b). k/s is the solution of the KUBELKA-MUNK-function, $F(R_\infty)$, wherein k = absorption coefficient and s = scattereing coefficient. For compositions of samples see Table 1.

Table 2. Crystallochemical aspects of phyllosilicates and of Cr³⁺-accomodation therein, as well as related spectroscopic parameters of this $3d^N$-ion accomodated in octahedra of phyllosilicate structures. Abbreviations: t = tetrahedral layer, o = octahedral layer attached to t, $o^{il.}$ = octahedral interlayer ("brucite type" layer $[M(OH)_6]$). The uncertainty in ν_1, 10Dq and CFSE is ca. $+40$ cm⁻¹ or $+0.5$ kJ/g-atom, resp., in ν_2 ca. $+80$ cm⁻¹ and in B ca. $+20$ cm⁻¹

Mineral	Type of layering	Cr³⁺ in octahedra of	Type of Cr³⁺-containing coordination octahedra	Mean octahedral distance, R_{M-O} [Å], R_{Cr-O}, EXAFS R_{M-O}, XRD	Cr₂O₃ content, wt%	Spectroscopic parameters of Cr³⁺[6]						
						ν_1 cm⁻¹	ν_2 cm⁻¹	10Dq cm⁻¹	B cm⁻¹	β	CFSE cm⁻¹	kJ/g-atom
Chromian clinochlore (kämmererite)	t-o-t, $o^{il.}$	$o^{il.}$, trioctahedral $[M_2^{2+}M^{3+}]$	$[M(OH)_6]$	$1.97^{(1)}$ $1.963^{(2)}$	7.47	18340	25170	18340	668	0.728	22010	263.8
Chromian amesite	t-o	o, trioctahedral $[M_2^{2+}M^{3+}]$	$[MO_2(OH)_4]$	— $2.03^{(3)}$	3.90	17820	24810	17820	694	0.756	21380	256.3
Chromium dickite	t-o	o, dioctahedral $[M_2^{3+}\square]$	$[MO_2(OH)_4]$	— $1.904^{(4)}$	$0.09^{(8)}$	16480	23870	16480	772	0.841	19780	237.1
Chromian smectite	t-o-t	o, dioctahedral $[M_2^{3+}\square]$	$[MO_4(OH)_2]$	— $1.96^{(1)}$	$17.5^{(1)}$	$16800^{(1)}$	$24000^{(1)}$	16800	738	0.804	$20160^{(1)}$	241.6
Chromian muscovite (fuchsite)	t-o-t	o, dioctahedral $[M_2^{3+}\square]$	$[MO_4(OH)_2]$	$1.97^{(1)}$ $1.95^{(5)}$	0.55	16200	23880	16200	826	0.899	19440	233.0
Chromian montmorillonite (volkonskoite)	t-o-t	o, di-/trioctahedral $[(M^{3+}, M^{2+})_{3-x}\square_x]$	$[MO_4(OH)_2]$	— $2.00^{(6)}$	21.05	16100	23200	16100	737	0.802	19320	231.6
Chromian phlogopite	t-o-t	o, trioctahedral $[M_3^{2+}]$	$[MO_4(OH)_2]$	— $2.07^{(3)}$	$1.24^{(9)}$	$16900^{(9)}$		$16900^{(9)}$			$20280^{(9)}$	243.1

[1]CALAS et al. (1984), [2]PHILLIPS et al. (1980), [3]WIEWIORA et al. (1991), [4]JOSWIG and DRITS (1986), [5]RULE and BAILEY in: BAILEY (1984), [6]this mean distance was estimated from Cr⁺⁶⁻O distances obtained by XRD refinements of a series of Cr-minerals near to end member compositions (e.g. eskolaite, magnesiochromite, uvarovite) on the basis of the fact that R_{M-O} in the respective (CrO₆)-octahedra themselves does not change much in series of solid solutions (LANGER, 1988; LANGER and GARSCHE, in prep.), [7]BAILEY (1984, Tab. 1), [8]CAO YUNGCHENG (1983), [9]KHOMENKO (personal communication, 1992).

Table 2 includes information on these characteristics for the minerals studied here. With respect to mean distances R, it should be pointed out that the values obtained in the refinement of X-ray diffraction data are crystal averaged and do not necessarily equal the local Cr—O distances. This is also indicated by the larger Cr—O EXAFS distances compared to the X-ray values in case of clinochlore and muscovite.

In Fig. 3, the values of the octahedral crystal field parameter $\Delta_o = 10Dq$ (Table 2) are plotted as a function of $1/R^5$ of eqn. (1). Where available, X-ray spectroscopic data on octahedral chromium-ligand distances were used to obtain $1/R^5$ (cf. Table 2). Where such local octahedral distances were not available, mean distances from X-ray diffraction refinements were used. We are aware that the local Cr-(O,OH) distances may be larger, in these cases, than quoted, because X-ray diffraction averages the distances in all the octahedra of one crystallographic type of site (cf. LANGER, 1988). It is obvious from Fig. 3 that there is indeed a $1/R^5$-proportionality of Δ_o. However, this is only valid when we are within one series of layer silicates, either the trioctahedral or the dioctahedral series. Between these two, there exists an extended gap of Δ_o. Thus, clinochlore and muscovite, with the same mean octahedral M^{3+}-O EXAFS distances of

1.97 A, show a difference in Δ_o of 2140 cm^{-1}, i.e. of more than 10%! In smectite only, the Δ_o-value of Cr^{3+} (CALAS et al., 1984) is anomalously high. The reason for this is not known.

This gap is obviously due to differences in the effective charge of the ligands, $Z_L \cdot e^2$ (cf. eqn. 1), coordinating the Cr^{3+}-ions in the structure of the minerals of the two series. The effective charges of hydroxyl and oxygen are different and, thus, OH is expected to create a weaker field than O^{2-} according to the spectrochemical series (BURNS, 1993), such that the Δ_o-values are expected to decrease in the sequence $CrO_4(OH)_2 > CrO_2(OH)_4 > Cr(OH)_6$ in accordance with point (ii) above. No such correlation is clearly demonstrated by the data in Table 2 and Fig. 3. Obviously, point (iii) predominantly accounts for the observed gap. This is consistent with the fact that Δ_o is generally lower in the dioctahedral minerals compared to the trioctahedral ones. Furthermore, the same ratio of hydroxyl to oxygen in the coordination sphere of chromium produces higher crystal field strength in trioctahedral than in dioctahedral minerals as is obvious from the pairs phlogopite/muscovite and amesite/dickite (cf. Tab. 2 and Fig. 3).

The second parameter dependent on the effective charge of the coordinating oxygens is the Racah parameter B and the nephelauxetic ratio, β, derived from it (see above). It was proposed (ABU-EID and BURNS, 1976; BURNS, 1993) that the value of B is larger in hydroxyl-bearing minerals than in those with O^{2-} as the coordinating ligands. The argument for this ist that the electron density at OH$^-$ is small compared to O^{2-}, such that the orbital overlap with the metal d-orbitals is smaller in the first case. This is also consistent with the nephelauxetic series (BURNS, 1993), from which a decrease in B and β is expected in the sequence $Cr(OH)_6 > CrO_2(OH)_4 > CrO_4(OH)_2$. However, the values of B and β derived from the spectra of the present study and listed in Table 3 show that the degree of covalency of the chromium-oxygen bond is higher in $Cr(OH)_6$ octahedra of clinochlore than in $CrO_4(OH)_2$ octahedra in muscovite. This shows that the effective charge on the oxygens attached to Cr^{3+} in the octahedral layer of muscovite is even smaller than that of hydroxyl ligands in the clinochlore interlayer. The reason may be that the four oxygen ligands per coordination polyhedron in the octahedral layer of muscovite and of the other 2:1-phyllosilicates, being the apices of the tetrahedral layers, are coordinated by tetrahedral $(Si_{4-x}Al_x)$. On the other hand, the hydroxyl ligands of the octahedral interlayer in clinochlore are not subject to such influence. That this consideration is likely to explain
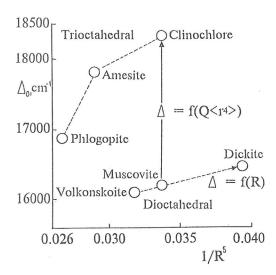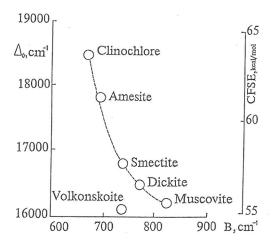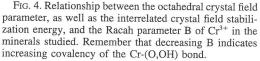

FIG. 3. Octahedral crystal field parameter, Δ_o, of Cr^{3+} in the phyllosilicates studied as a function of R^{-5} with R, the mean octahedral distance (see text). Note the large energy gap Δ between crystal field parameters in trioctahedral vs. dioctahedral phases. This gap is suggested to be caused by differences in the mean effective charge in case of trioctahedral members as compared to dioctahedral ones.

the unexpected behavior of B and β, is obvious from the fact that B and β in the 1:1 layer silicates, containing only two such oxygen ligands per coordination octahedron, have values between those in clinochlore and muscovite (Table 2).

Increasing covalency of the chromium-oxygen bond, as reflected by decreasing B- and β-values of $Cr^{3+[6]}$, is expected to be the result of increasing strength of the ligand field, *i.e.* of increasing crystal field parameter $\Delta_o = 10Dq$. Hence, there should exist a negative correlation between Δ_o and B. It is obvious that this is really the case in the minerals studied here. Fig. 4 quite clearly shows that the strength of the field, as reflected in $\Delta_o = 10Dq$, greatly determines the degree of covalency of the Cr^{3+}-(O,OH)-bonds as reflected in the values of Racah-parameter B. Only the data of volkonskite do not fit into the correlation of Fig. 4. Here, Δ_o is too low possibly as a result of the exceptionally high chromium concentration (Table 1) and the relatively large chromium-oxygen distance resulting from that.

CONCLUSION

The $1/R^5$-proportionality of the octahedral crystal field parameter $\Delta_o = 10Dq$ is confirmed for octahedral chromium in phyllosilicates only when either trioctahedral or dioctahedral layers are considered. Between the $\Delta_o = f(1/R^5)$-relations for the tri- or di-octahedral series, respectively, there occurs a broad energy gap which is probably due

to next-neighbor influences on the donor properties of the coordinating ligands. The nature of O^{2-} or OH^-, seems to play a minor role, an unexpected result when considering the position of the two types of ligands within the spectrochemical series (BURNS, 1993). Racah-parameter B was found to be negatively correlated with $\Delta_o = 10Dq$, a result that clearly demonstrates an increase of the covalency of the Cr^{3+}-(O,OH)-bonds with increasing strength of the crystal field.

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FIG. 4. Relationship between the octahedral crystal field parameter, as well as the interrelated crystal field stabilization energy, and the Racah parameter B of Cr^{3+} in the minerals studied. Remember that decreasing B indicates increasing covalency of the Cr-(O,OH) bond.

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