MgAl$_2$O$_4$:Cr$^{3+}$ and emerald display a different colour but the local symmetry is the same: Microscopic origin

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Abstract

The difference in colour between emerald (Be$_3$Si$_6$Al$_2$O$_{18}$:Cr$^{3+}$, green) and the Cr$^{3+}$-doped spinel MgAl$_2$O$_4$ (red) is striking, considering that in both systems colour is due to CrO$_6^{9-}$ complexes with D$_3$ symmetry and the measured Cr$^{3+}$-O$^{2-}$ distance is practically the same (1.98 ± 0.01 and 1.97 ± 0.01 Å, respectively). By means of density functional calculations it is shown that this surprising difference can reasonably be explained once the electric field, $E_R$, which all lattice ions lying outside the CrO$_6^{9-}$ complex exert on localized electrons, is taken into consideration. The origin of the different shape of $E_R$ in the two host lattices is analysed in detail. It is shown that $E_R$ raises (decreases) the 2p(O) levels for Be$_3$Si$_6$Al$_2$O$_{18}$:Cr$^{3+}$ (MgAl$_2$O$_4$:Cr$^{3+}$) along the trigonal axis thus favouring a decrease (increase) of 10Dq. The present work demonstrates the key role played by $E_R$ (not considered in the traditional ligand field theory) for understanding the differences exhibited by the same complex embedded in host lattices which do not have the same crystal structure. Some remarks on the colour of Cr$_2$O$_3$ pure compound are also reported.
1. Introduction

A great deal of experimental work has been devoted to look into the properties of gemstones and minerals involving Cr$^{3+}$-doped oxides\(^1\)-\(^3\). Despite these efforts the actual origin of the colour exhibited by the different oxides lattices containing Cr$^{3+}$ is still being debated\(^3\)-\(^10\).

Historically, the optical properties of gemstones like ruby (Cr$^{3+}$-doped corundum, Al$_2$O$_3$) and emerald (Cr$^{3+}$-doped beryl, Be$_3$Si$_6$Al$_2$O$_{18}$) have been interpreted in the framework of the traditional ligand field theory (LFT)\(^11\),\(^12\). In this domain, it is assumed that the electronic properties of a transition metal impurity, M, placed in an insulating lattice can be understood considering only the MX$_N$ complex formed with the N nearest ions or ligands, X. The fact that crystal-field spectra of KM$\text{M}M$$_3$ (M = Ni, Mn) pure compounds look very similar to those measured for KM$\text{M}M$$_3$:M$^{2+}$ (M = Ni, Mn) support such an assumption\(^13\)-\(^15\). Along this line theoretical calculations on NiF$_6^{4-}$, MnF$_6^{4-}$, CrF$_6^{3-}$ or CrO$_4^{4-}$ complexes in vacuo at the right experimental distance\(^16\)-\(^20\) is known to give values of optical transitions and electron paramagnetic resonance (EPR) parameters which are not far from experimental data\(^13\)-\(^15\),\(^21\),\(^22\) for KM$\text{M}M$$_3$:M$^{2+}$ (M = Ni, Mn), K$_2$NaGaF$_6$:Cr$^{3+}$ or Mg$_2$SiO$_4$: Cr$^{4+}$.

If the idea of complex is fully right the optical properties of an octahedral MX$_N$ complex embedded in a series of different host lattices would depend only on the actual value of the equilibrium metal-ligand distance. This statement has been verified to be right looking at the different optical spectra of MnF$_6^{4-}$, NiF$_6^{4-}$ and CrF$_6^{3-}$ complexes located in a series of distinct but isomorphous host lattices\(^23\)-\(^25\).

By virtue of these facts the red and green colour exhibited by ruby and emerald, respectively, have often been ascribed to a different value of the mean equilibrium Cr$^{3+}$-O$^{2-}$ distance, R$_I$, in the CrO$_6^{9-}$ complex\(^1\),\(^2\),\(^26\). Recent extended X-ray absorption fine structure (EXAFS) measurements carried out on ruby and emerald prove\(^3\),\(^4\),\(^6\),\(^9\) however that the R$_I$ value for both gemstones is the same within ±0.01 Å.
The colour of insulating oxides doped with Cr\(^{3+}\) essentially depends on the energy of the
first spin allowed transition \(4A_{2g} (t_{2g}^3) \rightarrow 4T_{2g} (t_{2g}^2 e_g)\) transition\(^{11}\) which is just equal to
the cubic field splitting parameter, 10Dq. Within the traditional LFT it is assumed that

\[
10Dq = (10Dq)_v
\]

where \((10Dq)_v\) stands for the complex in vacuo. Furthermore, it is assumed that \((10Dq)_v\)
for a given complex only depends on the metal-ligand distance, \(R\), through the law

\[
10Dq = CR^{-n}
\]

where \(C\) is a constant. Optical absorption measurements under hydrostatic pressure
carried out for \(\text{Al}_2\text{O}_3:\text{Cr}^{3+}\) have shown\(^{27}\) that experimental 10Dq values are reproduced
by Eqs. (1) and (2) with \(n = 4.5\). Similar results have been obtained for other transition
metal complexes\(^{12,15}\). The microscopic origin of the strong dependence of \((10Dq)_v\) upon
\(R\) has previously been discussed\(^{12,19,28,29}\). Bearing in mind these facts it is thus not
possible to conciliate the optical and structural data for ruby and emerald with the usual
view provided by the LFT.

A solution for understanding this somewhat puzzling situation has recently been put
forward\(^{5,7,10}\). It has been argued that even if active electrons are well localized in the
complex it should also be taken into consideration the electric field, \(E_R\), created by all
ions of the insulating lattice lying outside the complex, on the electrons in the complex.
The internal field \(E_R\) should, in principle, be present for every insulating lattice
composed by ions. This means that all properties (and thus 10Dq) associated with a
complex do also depend on the shape of \(E_R\) in the complex region. In particular it has
been emphasized the importance of incorporating \(E_R(r)\) when comparing the properties
of the same complex placed in two host lattices which are not isomorphous.

According to this new standpoint a difference between ruby and emerald comes out
merely considering the local symmetry around the Cr\(^{3+}\) impurity. In fact, in \(\text{Al}_2\text{O}_3:\text{Cr}^{3+}\)
the local symmetry is \(C_3\) and thus there is an electric field at the chromium site placed at
\(r = 0\). However, in the case of emerald \(E_R(0)\) is rigorously null as a result of a higher
local symmetry \(D_3\).
A more subtle problem has recently been raised\(^8\) in the comparison of emerald (\(\text{Be}_3\text{Si}_6\text{Al}_2\text{O}_{18}:\text{Cr}^{3+}\)) with the spinel MgAl\(_2\)O\(_4\) doped with Cr\(^{3+}\). In both cases the Cr\(^{3+}\) impurity enters the Al\(^{3+}\) site and the symmetry of the CrO\(_6^{9-}\) complex is D\(_3\). Recent EXAFS measurements\(^8,9\) have lead to a \(R_I = 1.97 \pm 0.01\) Å value for emerald while \(R_I = 1.98 \pm 0.01\) Å for MgAl\(_2\)O\(_4\):Cr\(^{3+}\). In spite of these facts the energy of the first spin allowed \(^4\!A_{2g} (t_{2g}^3) \rightarrow ^4\!T_{2g} (t_{2g}^2e_g)\) transition has been measured\(^1,30,31\) to be equal to 18520 cm\(^{-1}\) for MgAl\(_2\)O\(_4\):Cr\(^{3+}\) while it is equal only to 16130 cm\(^{-1}\) for Be\(_3\)Si\(_6\)Al\(_2\)O\(_{18}\):Cr\(^{3+}\). This means that, although emerald and the spinel MgAl\(_2\)O\(_4\) doped with Cr\(^{3+}\) share the same local symmetry and have practically the same \(R_I\) value, the colour displayed by MgAl\(_2\)O\(_4\):Cr\(^{3+}\) is red (identical to that of ruby for the human eye\(^26\)) and not green.

The present work is aimed at clarifying this relevant issue by means of the same procedure previously employed\(^5,7\) in the study of ruby, emerald and the two centres (with C\(_s\) and C\(_i\) symmetries) formed in alexandrite (BeAl\(_2\)O\(_4\):Cr\(^{3+}\)). Accordingly, 10D\(_q\) is derived by means of density functional calculations, considering the CrO\(_6^{9-}\) complex at the right equilibrium geometry and subject to the internal field, \(E_R(r)\), coming from the MgAl\(_2\)O\(_4\) host lattice. For well clearing out the origin of differences between MgAl\(_2\)O\(_4\):Cr\(^{3+}\) and emerald particular attention is paid to look into the shape of \(E_R(r)\) in the two MgAl\(_2\)O\(_4\) and Be\(_3\)Si\(_6\)Al\(_2\)O\(_{18}\) host lattices.

2. Computational Details

Calculations have been performed in the framework of the density functional theory (DFT) by means of the Amsterdam density functional (ADF) code\(^32\). All results shown in this paper have been performed on CrO\(_6^{9-}\) clusters at their experimental equilibrium geometries. For both systems, 10D\(_q\) has been computed for the complex \textit{in vacuo} as well as including the effects of the electrostatic potential, \(V_R(r)\), generating \(E_R\) through the relation \(E_R(r) = -\nabla V_R(r)\). The effects of \(V_R(r)\) have been included by means of the same technique described in previous works\(^5,7\).

The same functional and basis set are employed for calculating the emerald and the spinel. The generalized gradient approximation (GGA) exchange-correlation energy was computed using the Perdew-Wang functional\(^33\), PW91. It was verified that main results obtained in the present calculations are almost independent on the used
functional. The Cr$^{3+}$ ion has been described through basis sets of TZP (triple-$\zeta$ Slater-type orbitals STO plus one polarization function) quality given in the program database, keeping the core electrons (1s-3p) frozen. In the case of O$^{2-}$ ions, a DZP (double-$\zeta$ Slater-type orbitals STO plus one polarization function) basis sets quality has been used, keeping the 1s shell frozen. This is the description for oxygen ions which has provided better agreement with experimental findings in recent works.$^{5,7,34}$

The 10Dq parameter has been derived following the average of configuration procedure$^{35}$ based on Slater’s transition state concept$^{36}$. In the case of cubic symmetry the Kohn-Sham equations are solved for the t$_{2g}^{9/5}$e$_{g}^{6/5}$ configuration where all mainly d-levels are equally populated. As shown in Ref. [35], the difference between the $\varepsilon$(e$_{g}$) and $\varepsilon$(t$_{2g}$) eigenvalues derived for such configuration with fractional occupation leads to a reasonable 10Dq value. This procedure can easily be extended if the symmetry of the complex is lower than O$_{h}$, such as it happens in the present cases.

3. Results and Discussion

Seeking to look into the influence of the internal $E_R(r)$ field on 10Dq and the colour of MgAl$_2$O$_4$:Cr$^{3+}$ and emerald gemstones, calculations have been carried out in two steps. In the first one, 10Dq has been derived for the D$_3$ CrO$_6$$^{9-}$ complex in vacuo at the experimental equilibrium geometry thus considering the effects of small trigonal distortions. In a second step, the action of the internal electric field, $E_R(r)$, upon active electrons in the complex is incorporated into the calculation. Main results are collected in Table 1. In order to show the strong dependence of 10Dq upon R, calculated values for MgAl$_2$O$_4$:Cr$^{3+}$ at a distance $R = 1.995$ Å, very close to the experimental figure$^8$ $R_I = 1.98 \pm 0.01$ Å, have also been included in Table 1. For the sake of completeness in that table results for ruby are also reported, while values of the average Al$^{3+}$-O$_2^-$ distance in the perfect host lattices$^{4,8,37}$, $R_H$, are enclosed for comparison purposes.

It is worth noting that for emerald and the spinel the six Cr$^{3+}$-O$_2^-$ distances are equal although O$^{2-}$-Cr$^{3+}$-O$^{2-}$ angles do not correspond to a perfect octahedron$^{4,8,9,37}$. The departure from octahedral geometry is bigger for emerald than for MgAl$_2$O$_4$:Cr$^{3+}$. For instance, for two O$^{2-}$ ions in trans position the O$^{2-}$-Cr$^{3+}$-O$^{2-}$ angle is equal to 170.5° in the case of emerald while equal to 180° for spinel. The existence of this trigonal distortion in the CrO$_6$$^{9-}$ complex leads to small differences in the calculated 10Dq values.
for emerald and MgAl$_2$O$_4$:Cr$^{3+}$ when only the complex in vacuo is considered. Let us call $\Delta_{SE} = 10Dq(MgAl_2O_4:Cr^{3+}) - 10Dq(emerald)$. As shown in Table 1 the calculated value for the complex in vacuo is $\Delta_{SE} \sim 300$ cm$^{-1}$ and thus it is eight times smaller than the experimental value $\Delta_{SE} = 2390$ cm$^{-1}$.

Looking at the results gathered in Table 1 it is also hard to understand the distinct 10Dq values exhibited by MgAl$_2$O$_4$:Cr$^{3+}$ and emerald through the complex in vacuo even if the uncertainty in the experimental $R_I$ value (± 0.01 Å) is considered. In fact, as $R_H = 1.93$ Å for the spinel while $R_H = 1.906$ Å for beryl, it can reasonably be expected that $R(R_{MgAl_2O_4:Cr^{3+}}) \geq R(I)$ (emerald) according to the general behaviour observed when a given complex is inserted in different host lattices$^{12,23}$. In fact, for 3d complexes placed in a series of cubic insulating lattices it has been found that $R_I$ values are ordered in the same way as $R_H$. Bearing in mind these facts, Eq. (1) and the results of Table 1 it can be concluded that if we only consider the complex in vacuo $\Delta_{SE}$ is expected to be smaller than 300 cm$^{-1}$.

As shown in Table 1, a significant increase on the calculated 10Dq value of MgAl$_2$O$_4$:Cr$^{3+}$ is obtained once the corresponding internal electric field, $E_R(r)$, is incorporated into the calculation. In agreement with what was previously reported$^{5,7}$, $E_R(r)$ is found to reduce but only by $\sim 450$ cm$^{-1}$ the 10Dq value derived for emerald using a complex in vacuo. Therefore, the variation on 10Dq induced by $E_R(r)$ in this gemstone has a different sign to that in MgAl$_2$O$_4$:Cr$^{3+}$. These results just mean that when the complex is inserted in a lattice there is a supplementary contribution to 10Dq coming from $V_R(r)$, termed as $\Delta_R$, and Eq. (1) has to be modified to$^{10}$

$$10Dq = (10Dq)_v + \Delta_R$$

(3)

It has recently been pointed out that $\Delta_R$ plays a relevant role even if host lattices are cubic$^{38}$. The results gathered in Table 1 then support that the internal $E_R(r)$ field plays a key role for understanding why MgAl$_2$O$_4$:Cr$^{3+}$ is red despite the local symmetry around Cr$^{3+}$ is $D_3$, the same as for emerald. Despite this fact the results embodied in Table 1 and those previously obtained$^{5,7,38}$ stress that the main contribution to 10Dq comes from $(10Dq)_v$. 

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An insight into the origin of such a difference can be gained looking at Fig. 1, where the arrangement of neighbour ions to the CrO$_6^{9-}$ complex can be seen for both MgAl$_2$O$_4$ and Be$_3$Si$_6$Al$_2$O$_{18}$ host lattices. In both cases the direction called $d_1$ in Fig. 1 corresponds to the C$_3$ axis in D$_3$ symmetry. Despite the local symmetry around Cr$^{3+}$ is the same in both lattices the nature and arrangement of first and second shell of ions looks certainly different. In the case of MgAl$_2$O$_4$ the second shell around the central Al$_{c}^{3+}$ ion (which is replaced by the Cr$^{3+}$ impurity) is composed by six Al$^{3+}$ ions placed at 2.86 Å, while the third shell is formed by two O$^{2-}$ ions lying at 3.33 Å. All these ions are shown in Fig. 1. Next there are six Mg$^{2+}$ located at 3.35 Å and six O$^{2-}$ ions at 3.56 Å while further shells are all lying at a distance higher than 4 Å. Differences between the local geometry in MgAl$_2$O$_4$ and Be$_3$Si$_6$Al$_2$O$_{18}$ are already visible looking at the second shell. In fact, in Be$_3$Si$_6$Al$_2$O$_{18}$ there are only three Be$^{3+}$ ions lying at 2.66 Å from the central Al$_{c}^{3+}$ ion involved in this shell$^{4,9}$. Further differences between two lattices appear considering the angle, $\phi_3$, formed by an Al$_{c}^{3+}$ - M$_{2s}^{3+}$ direction with the principal C$_3$ axis. Here M$_{2s}^{3+}$ just means a cation of the second shell. While $\phi_3 = 90^\circ$ for beryl lattice, $\phi_3$ is equal only to 35.26$^\circ$ for the spinel. As shown in Fig. 1 six Si$^{4+}$ ions, at 3.28 Å from Al$_{c}^{3+}$, are involved in the third shell of Be$_3$Si$_6$Al$_2$O$_{18}$. The fourth sell is composed by six O$^{2-}$ ions at 3.73 Å from Al$_{c}^{3+}$.

Bearing in mind the structural differences between the spinel and the beryl lattices let us now have a look to the form of the calculated $E_R$ field in the two lattices. For seeing in what places of the complex region there is an electric field $E_R(\mathbf{r}) \neq 0$ it is useful to portray the potential $V_R(\mathbf{r})$ generating $E_R$. The form of the $(-e)\{V_R(\mathbf{r}) - V_R(0)\}$ function along several directions is drawn for both lattices in Fig. 2. For clarifying what are the chosen directions and specially the nature of involved electronic orbitals it is convenient to work also with the trigonal basis $\{x_t,y_t,z_t\}$ defined in Fig. 3. Quantities referred to this basis will be denoted by the subscript $t$.

In Fig. 2 the form of $(-e)V_R(\mathbf{r})$ is depicted for directions called $d_0$, $d_1$ and $d_2$. Here $d_1$ and $d_2$ correspond to $<0,0,1>_t$ and $<-1,1,\sqrt{2}>_t$ directions, respectively, while $d_0$ refers to a metal-ligand direction corresponding to $<1,0,0>_t$ type directions in the $\{x,y,z\}$ basis set (Fig. 3). These directions will be useful in the later discussion.
Although, according to D$_3$ symmetry, $E_R(0) = 0$ for both host lattices the shape of $(-e)V_R(r)$ looks quite different at the ligand region (Fig. 2). For instance, along the $d_1$ direction of Be$_3$Si$_6$Al$_2$O$_{18}$ the $(-e)V_R(r)$ function shows an increase of about 1 eV from the origin to the $r = (0,0,1)$ Å point, while for MgAl$_2$O$_4$ there is a lessening of 3 eV. As regards a metal-ligand direction, $d_0$, $(-e)V_R(r)$ decreases but slightly for beryl while it is practically flat for the spinel. The distinct shape of $(-e)V_R(r)$ along $d_1$ is qualitatively consistent with the quite different value of the $\phi_3$ angle for MgAl$_2$O$_4$ and Be$_3$Si$_6$Al$_2$O$_{18}$.

Considering the spinel lattice, if the electron moves from the central position along a $<0,0,1>$ direction it is attracted towards the closer plane of three Al$^{3+}$ ions (Fig. 1). By contrast, in beryl the three Be$^{3+}$ ions of the second shell are lying in a plane perpendicular to the $d_1$ direction (C$_3$ axis) and thus $(-e){V_R(r) - V_R(0)}$ should behave in an opposite way.

The different 10Dq values exhibited by MgAl$_2$O$_4$:Cr$^{3+}$ and emerald can qualitatively be understood just considering the effects of $(-e)V_R(r)$ upon $e_g (~x^2-y^2, 3z^2-r^2)$ and $t_{2g} (~xy, xz, yz)$ orbitals in first-order perturbation. In fact, at least ~80% of the 10Dq value is already obtained through a calculation of the complex in vacuo (Table 1).

Let us firstly consider the antibonding $e_g (~x^2-y^2, 3z^2-r^2)$ orbitals in cubic symmetry. It should be recalled here that although such orbitals transform like $x^2-y^2$ and $3z^2-r^2$ wavefunctions of central cation the actual molecular orbital wavefunctions involves an admixtures with 2p and 2s wavefunctions of oxygen ligands. As the degeneracy in $e_g$ is not removed by a trigonal distortion we can consider that in the present cases such orbitals describe in a first approximation the $e$ orbitals in D$_3$ symmetry. Bearing in mind that $e_g (~x^2-y^2, 3z^2-r^2)$ orbitals are mainly directed towards ligands ($d_0$ directions) and looking at Fig. 2, it can be expected that $E_R$ has practically no effect for MgAl$_2$O$_4$:Cr$^{3+}$ while it would induce a decrease of the energy of such orbitals in the case of the emerald thus favouring a lessening of 10Dq. It should be remarked that, in order to interpret Fig. 2, such effect depends on the probability of finding an $e_g$ electron on ligands and thus on the covalency of the chemical bonding between chromium and oxygen ligands. Present calculations give a total charge on ligands equal to 25% (14%) for an electron in an $e_g$ ($t_{2g}$) orbital.
More interesting effects appear precisely in the case of $t_{2g}$ ($\sim xy, xz, yz$) orbitals in cubic symmetry. First of all the trigonal distortion splits $t_{2g}$ into a singlet $a$ and a doublet $e$. The wavefunction of the $a$ singlet transforms like $(xy + xz + yz)$, that is, $3z^2 - r^2$ in the trigonal basis (Fig. 3). This means that the $a$ orbital is directed along the C3 axis although some density is also located in the perpendicular plane (Fig. 4). As regards the $e(t_{2g})$ doublet the two orbitals forming the basis can be chosen as $(xz - yz) \sim (\sqrt{2}xy + xz + yz)$ and $(xz + yz - 2xy) \sim (x^2 - y^2 + \sqrt{2}yz)$. Considering the $(xz - yz) \sim (\sqrt{2}xy + xz)$ orbital of the $e(t_{2g})$ doublet it involves an admixture of the $xy$, orbital, lying in the perpendicular plane to the C3 axis, with the $xz$, lying outside that plane. The $(xz - yz) \sim (\sqrt{2}xy + xz)$ orbital possesses four lobes, two placed along $<-1,1,\sqrt{2}> = <\sqrt{3},\sqrt{2},1>$ and two along $<1,-1,\sqrt{2}> = <-\sqrt{3},\sqrt{2},1>$ direction. Bearing in mind these considerations it is possible to understand the different influence of $(-e)V_R(r)$ on $t_{2g}(xy, xz, yz)$ orbitals in the two host lattices. Let us first consider the $a(t_{2g})$ orbital. Looking at Figs. 2 and 4 it is clear that in the case of emerald the electronic density lying around $<0,0,1>$ increases its energy due to the action of $V_R(r)$. By contrast, for the spinel the electronic density located in the neighbourhood of $r = <0,0,1.5>$ Å is subject to $(-e)\{V_R(r)- V_R(0)\} \approx -3$ eV, which tends to decrease the energy of the $a(t_{2g})$ orbital. In Fig. 2 is also portrayed the form of $V_R(r)$ along a $d_2$ direction corresponding to one of the lobes of the $(xz - yz) \sim (\sqrt{2}xy + xz)$ orbital. It can be noticed that for both MgAl$_2$O$_4$:Cr$^{3+}$ and emerald $(-e)V_R(r)$ is practically constant for $|r| < 1.5$ Å, although it increases slightly for higher distances. In view of these considerations, it can be expected that the energy of the $t_{2g}$ barycentre of the emerald is increased with respect to that of the spinel due to the action of the internal electric field. This fact helps again to lessen the value of 10Dq in the former case and to enhance it in the latter one. The present argument is thus in qualitative agreement with the calculated values shown in Table 1.

3. Final Remarks

The present study shows that the different colour of MgAl$_2$O$_4$:Cr$^{3+}$ and emerald can be well explained considering the CrO$_6^{9-}$ complex subject to the corresponding internal field $E_R$. This result is thus consistent with recent findings showing that the shift undergone by crystal-field and charge transitions of Cr$^{3+}$ and Fe$^{3+}$ impurities on passing
from beryl to corundum can also be ascribed to the different shape of $E_R$ in the two host lattices$^{39}$.

Although the local symmetry around the impurity is the same in MgAl$_2$O$_4$:Cr$^{3+}$ and emerald, however the arrangement of close ions and consequently the behaviour of $V_R(r)$ is quite different in both lattices as stressed by Figs. 1 and 2. It is worth remarking here that the importance of $V_R(r)$ in the present problem is enhanced due to the directionality of orbitals. By virtue of this fact, the electronic density in $e_g$ and $t_{2g}$ orbitals is not isotropically distributed in the complex region.

The present calculations gathered in Table 1 lead to a 10Dq value for MgAl$_2$O$_4$:Cr$^{3+}$ which is higher than that for ruby. Although this is in qualitative agreement with experiments$^{1-3,30,31}$, the observed difference in 10Dq between both systems, $\Delta_{SR}$, is only of 450 cm$^{-1}$, and thus this difference is overestimated by the present calculations leading to $\Delta_{SR} = 2600$ cm$^{-1}$ using $R_1 = 1.98$ Å for MgAl$_2$O$_4$:Cr$^{3+}$ (Table 1). Apart from the fact that discrepancies between experimental and calculated 10Dq values of about 1000 cm$^{-1}$ are very common, there are two factors that could contribute to reduce this overestimation. On one hand, if there is an experimental uncertainty of $\pm 0.01$ Å for each system this could lead to a decrease of 1000 cm$^{-1}$ in $\Delta_{SR}$. On the other hand, the calculated splitting between $e(t_{2g})$ and $a(t_{2g})$ orbitals for MgAl$_2$O$_4$:Cr$^{3+}$ is $\sim 2600$ cm$^{-1}$ which is not observed experimentally. We have verified that this splitting is greatly due to a 25% contamination of 4s orbitals in the singlet $a(t_{2g})$ which lies below $e(t_{2g})$. If this anomaly is eliminated this would decrease 10Dq by $\sim 600$ cm$^{-1}$.

The present results underline that the difference $\Delta_{SE}$ can reasonably be understood considering the effects of the corresponding $V_R(r)$ potential in first-order perturbation. As it has been previously underlined the situation can be more complex in the case of ruby. It has been argued$^5$ that due to the existence of an electric field along the whole metal-ligand direction it can give rise to more important changes in the electronic density with respect to what is found for the complex in vacuo.

Let us now say a few words on the green colour displayed by the Cr$_2$O$_3$ pure compound$^{40}$ which has the same structure as Al$_2$O$_3$. Compared to Al$_2$O$_3$:Cr$^{3+}$ (10Dq = 18070 cm$^{-1}$), the value 10Dq = 16700 cm$^{-1}$ measured for Cr$_2$O$_3$ involves a shift $\Delta$(10Dq)
-1370 cm\(^{-1}\). Recent EXAFS measurements\(^6\) give a mean distance \(R_I = 1.965 \pm 0.01\) Å for ruby while \(R_I = 1.98 \pm 0.01\) Å for \(\text{Cr}_2\text{O}_3\). According to Eq. (2), one would expect that on going from \(\text{Al}_2\text{O}_3:\text{Cr}^{3+}\) to \(\text{Cr}_2\text{O}_3\) the \((10\text{Dq})_v\) quantity would decrease by \(-600\) cm\(^{-1}\). Nevertheless, this figure is about half the experimental value \(\Delta(10\text{Dq}) = -1370\) cm\(^{-1}\). It is worth noting however that while in \(\text{Al}_2\text{O}_3\) the charge on aluminium is found\(^41\) to be practically equal to +3 the charge on chromium in \(\text{Cr}_2\text{O}_3\) is expected to be smaller as a result of the covalent bonding which is always present in every transition-metal complex. As shown in Section 2, 14% of the electronic charge associated with an electron in an antibonding \(t_{2g}\) orbital is found to be placed on ligands. The expected reduction on the absolute value of metal and oxygen charges on passing from \(\text{Al}_2\text{O}_3\) to \(\text{Cr}_2\text{O}_3\) tends to decrease the value of \(|V_R(r) - V_R(0)|\) and thus the \(\Delta_R\) contribution. Along this line, it has been shown\(^5\) that if in the \(\text{Al}_2\text{O}_3\) lattice the cation charge goes from +3 to +2.7 it induces a \(\Delta_R\) lessening of 550 cm\(^{-1}\). Work on this subject is currently under way.

**Acknowledgments**

The authors would like to thank to A. Juhin who suggested to explore the present problem. The support by the Spanish Ministerio de Ciencia y Tecnología under Project FIS2006-02261 is acknowledged.

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| System            | $R_H$  | $R$  | 10Dq in vacuo | 10Dq under $E_R$ | Experimental |
|-------------------|--------|------|---------------|-----------------|--------------|
| Emerald           | 1.906  | 1.975 | 16188         | 15739           | 16130        |
| MgAl$_2$O$_4$:Cr$^{3+}$ | 1.930  | 1.980 | 16336         | 20627           | 18520        |
| Ruby              | 1.913  | 1.965 | 16043         | 18179           | 18070        |

**Table 1.** Calculated 10Dq values for the CrO$_6^{9-}$ complex *in vacuo* (at the experimental equilibrium geometry$^{4,8,9}$) and under the internal electric field, $E_R$, coming from Be$_3$Si$_6$Al$_3$O$_{18}$, MgAl$_2$O$_4$ and Al$_2$O$_3$ host lattices. The experimental 10Dq values of these systems$^{1,4,30,31}$ are also enclosed. In the case of MgAl$_2$O$_4$:Cr$^{3+}$, 10Dq is given for the experimental distance$^8$ ($R_I = 1.98 \pm 0.01$ Å) and also for $R = 1.995$ Å. In the case of ruby, $R_I$ and $R_H$ mean the average Cr$^{3+}$-O$^{2-}$ and Al$^{3+}$-O$^{2-}$ distance respectively. $R$ and $R_H$ are given in Å while 10Dq in cm$^{-1}$. 

Figure captions

Figure 1. (Color online) CrO$_6^{9-}$ complexes and their surrounding shells of neighbours in (a) the emerald and (b) in the spinel. The meaning of the directions d$_1$ and d$_2$ is explained in the text and in the Fig. 3.

Figure 2. (Color online) (a) Electrostatic potential $V_R(r)$ of the rest of the lattice ions on a CrO$_6^{9-}$ complex for the case of emerald (above) and spinel (below), depicted along d$_0$, d$_1$ and d$_2$ directions. The meaning of the three directions is explained in the text and in the Fig. 3.

Figure 3. (Color online) Main axis of an octahedral basis $\{x,y,z\}$ and in a trigonal basis $\{x_t,y_t,z_t\}$ related by $x_t = \frac{1}{\sqrt{2}}(-x+y)$, $y_t = \frac{1}{\sqrt{6}}(-x-y+2z)$, $z_t = \frac{1}{\sqrt{3}}(x+y+z)$. d$_1$ and d$_3$ directions coincide with $z_t$ and $x_t$, respectively, while d$_2$ is written as $d_2 = \frac{1}{2}x + \frac{1}{2}y + \frac{1}{\sqrt{2}}z$ in the octahedral basis or equivalently $d_2 = \frac{1}{\sqrt{2}}x_t + \frac{1}{\sqrt{3}}y_t + \frac{1}{\sqrt{6}}z_t$ in the trigonal basis.

Figure 4. (Color online) Orbitals belonging to the $t_{2g}$ triplet in a D$_3$ symmetry. (a) Singlet orbital $a$. It is written as $(xy + xz + yz)$ in the octahedral basis and $3z_t^2 - r_t^2$ in the trigonal basis. (b) First of the orbitals of the doublet $e$. It is written as $(xz - yz)$ in the octahedral basis and $(\sqrt{2}x_t y_t + x_t z_t)$ in the trigonal basis. (c) Second of the orbitals of the doublet $e$. It is written as $(xz + yz - 2xy)$ in the octahedral basis and $(x_t^2 - y_t^2 + \sqrt{2} y_z z_t)$ in the trigonal basis. The meaning of the directions d$_1$ and d$_2$ is explained in the text and in the Fig. 3.
Figure 1
Figure 4