Internal electric fields and color shift in Cr3+-based gemstones

Aramburu, J. A.; Garcia-Fernandez, P.; García Lastra, Juan Maria; Barriuso, M. T.; Moreno, M.

Published in:
Physical Review B (Condensed Matter and Materials Physics)

Link to article, DOI:
10.1103/PhysRevB.85.245118

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Internal electric fields and color shift in Cr$^{3+}$-based gemstones

J. A. Aramburu, P. García-Fernandez, J. M. García-Lastra, M. T. Barriuso, and M. Moreno

1Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain
2Center for Atomic-Scale Materials Design, Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
3Departamento de Física Moderna, Universidad de Cantabria, Avenida de los Castros s/n, 39005 Santander, Spain

(Received 16 February 2012; published 18 June 2012)

Seeking to better understand the origin of the different colors of emerald and ruby, both ab initio periodic and cluster calculations have been carried out. The calculations reproduce the interatomic distances measured for pure Be$_3$Si$_6$Al$_2$O$_{18}$ and Al$_2$O$_3$ as well as the Cr$^{3+}$-$O^{2-}$ distances in emerald and ruby. The mean Cr$^{3+}$-$O^{2-}$ distance for Be$_3$Si$_6$Al$_2$O$_{18}$ and Al$_2$O$_3$:Cr$^{3+}$ is found to be practically equal to 1.97 Å, in agreement with recent experimental values. The present calculations confirm that the variations of optical properties due to Cr$^{3+}$ impurities along the series of ionic oxides can be understood merely through the CrO$_6^{3-}$ unit but subject to the electric field due to the rest of the lattice ions. As a salient feature it is proved that changes in electronic density and covalency due to the internal field are not the cause of the color shift. Therefore, the red color of ruby is not due to the polarization of the electronic cloud around chromium as a result of the C$_3$ local symmetry. The electric field due to the rest of the lattice ions. As a salient feature it is proved that changes in electronic density and covalency due to the internal field are not the cause of the color shift. Therefore, the red color of ruby is not due to the polarization of the electronic cloud around chromium as a result of the C$_3$ local symmetry.

I. INTRODUCTION

The properties of oxides doped with Cr$^{3+}$ ions, like ruby (Al$_2$O$_3$:Cr$^{3+}$), emerald (Be$_3$Si$_6$Al$_2$O$_{18}$:Cr$^{3+}$), or alexandrite (BeAl$_2$O$_4$:Cr$^{3+}$), have raised a great deal of interest.3−22

Despite that in all oxides the Cr$^{3+}$ impurity is surrounded by an octahedron of oxygen ligands, the color exhibited by gemstones like ruby and emerald, however, is not the same.3,6

Historically, two main assumptions have been put forward for explaining such a difference. On one hand, some scientists have assumed that the mean Cr$^{3+}$-$O^{2-}$ distance, R, is not the same for gemstones like ruby and emerald.1,3,4,7,10,15,23 This idea relies on the fact that color is mainly determined by the energy of the $^4A_2(t_{2g}^2)\rightarrow^4T_2(t_{2g}^2e_g^1)$ spin allowed transition which is equal to the ligand field splitting parameter 10Dq.24

Moreover, 10Dq is known to be very sensitive to hydrostatic pressures and thus to changes of the metal-ligand distance.25,26

By contrast, many other authors have suggested that unpaired electrons are not fully localized on the CrO$_6^{3-}$ complex but are present in the second and further coordination spheres, which are not the same in ruby and emerald.2,25−29

According to this view the flow of electronic charge through the same mechanism.32,33 Furthermore, it has been shown that $E_R(r)$ plays a key role for understanding the local structure and the associated spectroscopic properties of Cu$^{2+}$- and Cr$^{3+}$-doped perovskites such as K$_2$Af$_4$ (A = Mg, Zn).39

Although the mere addition of the internal electric field $E_R(r)$ to the CrO$_6^{3-}$ complex allows one to understand an important number of experimental facts corresponding to the Cr$^{3+}$-based gemstones, there is, however, a fundamental question which needs to be answered. As it has been pointed out, the internal electric field $E_R(r)$ will modify the electronic density

DOI: 10.1103/PhysRevB.85.245118 PACS number(s): 71.55.–i, 71.15.Mb, 78.40.–q, 91.60.Mk
and covalency inside the CrO$_6^{3−}$ unit provided $V_0(\mathbf{r})$ is not a constant on the whole complex region. This conclusion follows directly from the Hohenberg-Kohn theorem.\cite{40} Therefore, it is of fundamental importance to clarify whether such changes of electronic density are or are not directly related to the changes in $10D_q$ which are in turn responsible for the color shift. This work is addressed to shed light on this relevant matter.

For achieving this goal, we have first explored two representative gemstones as ruby and emerald by means of $ab$ \textit{initio} calculations. Aside from deriving the equilibrium Cr$^{3+}$-O$^{2−}$ distances and the $10D_q$ value for both gemstones, particular attention is paid to look into the actual changes of electronic levels and the electronic density induced by $V_0(\mathbf{r})$. Bearing these results in mind, we investigate in a further step a model system where $V_R(\mathbf{r})$ keeps the cubic symmetry, thus making the analysis of results easier than for ruby or emerald where the local symmetry is $C_1$ and $D_3$, respectively.

This work is arranged as follows. As the present study is based on electron localization, the main facts supporting its validity are briefly reviewed in Sec. II. Relevant details of the employed $ab$ \textit{initio} methods are given in Sec. III. In Sec. IV the changes in electronic density due to the internal field $E_R(\mathbf{r})$ for ruby and emerald are quantified. Section V is addressed to quantify the shift in $10D_q$ parameter directly associated with electronic density changes in the case of the model system. Some final remarks are presented in the last section.

II. ELECTRON LOCALIZATION

It is well known that the crystal field spectra of pure compounds like Cr$_2$O$_3$ or KNiF$_3$ look rather similar to those observed for Al$_2$O$_3$:Cr$^{3+}$ or K MgF$_3$:Ni$^{2+}$,\cite{2,24,26} This fact strongly supports that in all these systems active electrons are essentially localized in the $MX_6^{9−}$ complex ($M = \text{Cr}^{3+}, \text{Ni}^{2+}$) formed with the six $X$ ligands ($X = \text{O}, \text{F}$). This conclusion is consistent with a general view by W. Kohn stressing that the charge of active electrons is essentially confined to a close aluminum ion. ENDOR results with the closest aluminum ions have been measured by ENDOR,\cite{47} showing that in all these systems active electrons are essentially localized in the ground state is the fingerprint of electron localization in the ground state.\cite{40} Therefore, it is of fundamental importance to clarify whether such changes of electronic density are or are not directly related to the changes in $10D_q$ which are in turn responsible for the color shift.

In a first step, periodic $ab$ \textit{initio} calculations based on the density functional theory (DFT) have been carried out on ruby and emerald in order to obtain the equilibrium geometries around the Cr$^{3+}$ impurities in both gemstones as well as values of the charges of the lattice ions. Calculations were performed with the \textsc{Crystal09} package that employs localized Gaussian basis sets to represent the Bloch orbitals.\cite{47} All ions have been described by all-electron basis sets of reasonably high quality (5–11G for Be, 8–11G$^*$ for O, 85–11G for Al, 88–31G$^*$ for Si, and 86–41G$^{**}$ for Cr) taken from the \textsc{Crystal} data base.\cite{48} In the case of emerald we have used the hexagonal cell of Be$_2$Si$_6$Al$_2$O$_{18}$ with 58 ions, where the Cr$^{3+}$ replaces an Al$^{3+}$ ion of the lattice, while for ruby we used a $2 \times 2 \times 2$ supercell with 80 atoms. We have treated the exchange and correlation of the electrons through the B1WC hybrid functional\cite{49} that allows geometry and band gaps to be obtained with great accuracy and reliability not requiring the input of any semiempirical parameter by the user. For checking the reliability of the employed method the equilibrium geometries of pure Al$_2$O$_3$ and Be$_2$Si$_6$Al$_2$O$_{18}$ lattices have also been calculated.

In a second step, molecular DFT calculations have been carried out on CrO$_6^{9−}$ complexes either isolated or merely subject to the electric field $E_R(\mathbf{r})$ generated by infinite point charges from the rest of the lattice. In all these cases the Cr$^{3+}$-O$^{2−}$ distances correspond to the actual values for ruby and emerald. As it has been discussed in the previous section, the great localization of the electrons of the impurity makes that this simple CrO$_6^{9−}$ unit, but subject to the electric field $E_R(\mathbf{r})$, it is enough to unveil the microscopic origin of the different optical properties displayed by Cr$^{3+}$ in a series of oxides or fluorides.\cite{11,12,17,34} Calculations have been performed by means of the \textsc{ADF} 2010.02 code.\cite{50} The generalized gradient approximation (GGA) exchange-correlation energy was computed according to the Perdew-Wang-91 functional.\cite{51} The core electrons ($1s-3p$ for Cr and $1s$ for O) were kept frozen. Chromium ion was described through the basis sets of TZP quality [triple-$ξ$ Slater-type orbital (STO) plus one polarization function], whereas a DZP basis set (double-$ξ$ STO plus one polarization function) was used for oxygen ions. It has been reported in previous works\cite{11,12,52} that in order to correctly represent the metal-ligand covalence in a cluster model it is necessary to use a smaller basis set size in the ligands than in the metal. For being sure about the reliability of our main conclusions, calculations with other basis sets and functionals have also been performed. As a salient feature the main effect introduced by $E_R(\mathbf{r})$ on $10D_q$ is always found for every employed basis set or exchange-correlation functional. It is worth noting that calculated properties are found to be less dependent on the basis set using DFT than traditional methods based on the Hartree-Fock description.\cite{53,54} $10D_q$ has always been calculated following the average of configuration procedure given in Ref. \textsc{55}. The center of gravity of the small splitting undergone by the $t_2g$ orbital under the trigonal site symmetry has been taken into account when deriving $10D_q$.

III. COMPUTATIONAL DETAILS

Some final remarks are presented in the last section.
In particular, assuming that 10Dq ∝ R−n, an exponent n = 4.2 has been found by means of these calculations. This figure is not far from the value n = 4.5 measured experimentally for ruby under hydrostatic pressure.5 The electrostatic potential V_\text{E}(r) coming from all ions of Al2O3 or Be3Si6Al2O18 crystals lying outside the CrO63− unit has been calculated by means of the Ewald method, following the procedure described in Ref. 56. The nominal ionic charges were employed in these calculations since our periodic calculations performed on Al2O3 and Be3Si6Al2O18 lattices have demonstrated that the total charges on oxygen, aluminum, beryllium, and silicon ions are practically equal to −2e, +3e, +2e, and +4e (e = proton charge), respectively, pointing out that bonding is highly ionic indeed. A similar conclusion was previously reached by Sousa et al. in their study of Al2O3.57

IV. RESULTS FOR RUBY AND EMERALD

A. Ruby

The structure of the Al2O3 host lattice9,36 is depicted on Fig. 1. A given Al3+ cation is surrounded by six O2− anions, three at a short distance R_s = 1.857 Å and the rest lying further at R_l = 1.969 Å. The local symmetry is C3. Along the C3 axis there are two Al3+ ions neighbors of a given aluminum ion. One called Al13+ is located at 2.65 Å, while the other called Al23+ is placed much further at 3.80 Å. In the plane perpendicular to the C3 axis there are three Al13+ ions lying at 2.79 Å. Such ions are called Al13+ in Fig. 1.

The formation of ruby implies the Al3+ → Cr3+ substitution. Due to the different ionic radius of Al3+ and Cr3+, this replacement is likely to modify the values of both R_s and R_l distances. The next section is focused on the actual R_s and R_l values when an Al3+ ion is replaced by Cr3+, as they are important for a right interpretation of optical data of ruby.

![Fig. 1. (Color online) Local structure of corundum Al2O3 around an Al3+ ion with a C3 symmetry. A given Al3+ cation is surrounded by six O2− anions, three O_1 at a short distance R_s = 1.857 Å and three O_2 lying further at R_l = 1.969 Å. Along the C3 axis there are two Al13+ ions neighbors of a given aluminum ion, one called Al13+ is located at 2.65 Å while the other called Al23+ is placed much further at 3.80 Å. In the plane perpendicular to the C3 axis there are three Al13+ ions lying at 2.79 Å.](image-url)

### Table I. Values of R_s and R_l distances (in angstroms) obtained in this work by means of periodic calculations for pure Al2O3. The values are compared to experimental data5,36 as well as to those previously calculated by Duan et al.58 and Mazurenko et al.29

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Duan et al.</th>
<th>Mazurenko et al.</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>R_s (Å)</td>
<td>1.868</td>
<td>1.839</td>
<td>1.85</td>
<td>1.857</td>
</tr>
<tr>
<td>R_l (Å)</td>
<td>1.976</td>
<td>1.969</td>
<td>1.98</td>
<td>1.969</td>
</tr>
</tbody>
</table>

1. Local structure in ruby

As a first step we have derived by means of periodic calculations the R_s and R_l values corresponding to the pure Al2O3 lattice. As shown in Table I the figures R_s = 1.868 Å and R_l = 1.976 Å are close to those previously obtained by Duan58 and coincident within 1 pm with the experimental values R_s = 1.857 Å and R_l = 1.969 Å.9,36

The calculated equilibrium R_s and R_l distances corresponding to ruby are given in Table II where they are compared to the experimental EXAFS values obtained by Gaudry et al.7 as well as to figures derived in previous calculations. Values found in the present calculations are reasonably close to the experimental figures R_s = 1.92 ± 0.01 Å and R_l = 2.01 ± 0.01 Å and support that the mean Cr3+...O2− distance in ruby is R_m = 1.97 Å, which is thus identical to that measured for emerald.13 It can also be seen in Table I that the metal-ligand distance values obtained in our calculations are very similar to those computed by other authors on the same 80-atom supercell but using different. However, unlike with previous calculations, all our calculations have been made using all-electron basis functions and hybrid functionals.

2. Effect of the internal electric field on 10Dq

The form of the electrostatic potential due to the rest of the lattice ions on the CrO63− complex V_\text{E}(r) for three particular directions in ruby is depicted in Fig. 2. So, the changes of V_\text{E}(r) along the Os−Cr−O_1 path (direction d_1), the diagonal joining the central Cr3+...impurity, one Al13+ cation (direction d_2), and finally the C3 axis (direction d_3) are all shown in Fig. 2.

As portrayed in Fig. 2, there is an electric field directed along the trigonal axis at the chromium site, a fact consistent with the C3 local symmetry. Figure 2 also indicates that if unpaired electrons would be rigorously placed at the position of the chromium nucleus, its energy would experience a decrease of about −54 eV due to the action of (−e)V_\text{E}(0).

However, if the unpaired electronic density spreads on the CrO63− complex, V_\text{E}(r) changes significantly in that region, as shown in Fig. 2. For instance, if r is varied along direction d_3, then (−e)V_\text{E}(r) = −85 eV when |r| = 2 Å and the electron is close to Al13+, while (−e)V_\text{E}(r) = −45 eV when it is at the same distance but in the opposite direction.

As shown in Fig. 3, the energy decrease induced by (−e)V_\text{E}(r) is different for t_2g and e_g antibonding orbitals. In fact, while the center of the gravity of e_g levels moves downward by 52.22 eV, this figure is slightly higher (52.48 eV) for the case of t_2g levels, such as depicted in Fig. 3. This difference, though tiny, produces an increase in the 10Dq value. Indeed, if 10Dq is calculated for the isolated CrO63− complex at the right equilibrium geometry in ruby but ignoring the effects of
TABLE II. Values of Cr$^{3+}$-$\text{O}^{2-}$ distances calculated by means of periodic calculations using an 80-atom supercell for Al$_2$O$_3$:Cr$^{3+}$. The $R_e$ and $R_i$ distances are compared to those measured by EXAFS (Ref. 9) and those derived by Duan et al. and Gaudry et al. through LDA Carr-Parinello methods, Mazurenko et al. with a LDA + U tight-binding linear-muffin-tin method, and Watanabe et al. with a GGA calculation.

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Present work</th>
<th>Duan et al.</th>
<th>Gaudry et al.</th>
<th>Mazurenko et al.</th>
<th>Watanabe et al.</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_e$ (Å)</td>
<td>1.942</td>
<td>1.918</td>
<td>1.95</td>
<td>1.93</td>
<td>1.922</td>
<td>1.92</td>
</tr>
<tr>
<td>$R_i$ (Å)</td>
<td>1.997</td>
<td>2.018</td>
<td>2.00</td>
<td>1.99</td>
<td>1.986</td>
<td>2.01</td>
</tr>
</tbody>
</table>

$V_R(r)$, a value of 10Dq = 2.00 eV is obtained (Fig. 3), which is smaller than the experimental figure 10Dq = 2.24 eV.$^{3,6}$ Nevertheless, as shown in Fig. 3, the action of $\langle -e \rangle V_R(r)$ on the CrO$_6^{9-}$ complex produces an increase of 10Dq of 0.24 eV that although small (12%), shifts the color of ruby from green to red. This conclusion is thus fully consistent with the results of a previous study.$^{11}$ Supporting this view a calculation carried out on a bigger CrO$_6$Al$_7$ unit are displayed in Table III. Results given together with previous data obtained by Gaudry et al.$^{13,37,38}$ The local symmetry is $D_3$, higher than in ruby, and all nearest $O^2-$ anions lie at the same distance $R = 1.903$ Å, as shown in Table IV. Thus, this value is only 0.01 Å smaller than the average Al$^{3+}$-$O^2-$ distance measured in Al$_2$O$_3$.

Results on the equilibrium geometry of beryl derived through periodic calculations are also collected in Table IV together with previous data obtained by Gaudry et al.$^{1,13}$ It can be noticed that in the antibonding $e_g$ level the unpaired electron spends more time on O$_3$ than on O$_1$ oxygens. As the opposite happens for the corresponding bonding orbital which is fully occupied, this implies that there is a net flow of electronic charge going from O$_3$ to O$_1$. This fact, similar to that discussed in LiBaF$_3$:Mn$^{2+}$,$^{3,32}$ is consistent with the closeness of Al$^{3+}$ to the three O$_1$ ligands (Fig. 1) and the form of $\langle -e \rangle V_R(r)$ along the $d_1$ direction, such as it is shown in Fig. 2.

**B. Emerald**

1. **Local structure in emerald**

The structure of beryl (Be$_2$Si$_6$Al$_2$O$_18$) around an Al$^{3+}$ ion is shown in Fig. 4.$^{13,37,38}$ The local symmetry is $D_3$, higher than in ruby, and all nearest $O^2-$ anions lie at the same distance $R = 1.903$ Å, as shown in Table IV. Thus, this value is only 0.01 Å smaller than the average Al$^{3+}$-$O^2-$ distance measured in Al$_2$O$_3$.

Results on the equilibrium geometry of beryl derived through periodic calculations are also collected in Table IV together with previous data obtained by Gaudry et al.$^{1,13}$ It can be noticed that all calculated $R$ values gathered in Table IV are coincident with the experimental values within 0.4%. Similarly the experimental distances between an Al$^{3+}$ ion and the three nearest Be$^{2+}$ ions (2.66 Å) and the six closest Si$^{4+}$ ions (3.26 Å) are reasonably reproduced by the calculations.

The replacement of an Al$^{3+}$ by a Cr$^{3+}$ impurity induces, as expected, a slightly outward relaxation, such as shown in Table V. The Cr$^{3+}$-$O^2-$ distance derived by the present calculations ($R = 1.968$ Å) is coincident within 0.4% with

**FIG. 2.** (Color online) Potential energy on an electron, $\langle -e \rangle V_R(r)$, due to the internal electric potential, $V_R(r)$, produced by the rest of the lattice ions of ruby on the CrO$_6^{9-}$ complex. Energy is depicted along the O$_3$-$\text{Cr}$-$O_1$ path (direction $d_1$), the diagonal joining the central Cr$^{3+}$ impurity, and one Al$^{3+}$ ion (direction $d_2$) and the $C_3$ axis (direction $d_3$).

**FIG. 3.** (Color online) Scheme depicting the energy decrease induced by the $\langle -e \rangle V_R(r)$ contribution for $t_{2g}$ and $e_g$ antibonding orbitals in ruby and emerald.
TABLE III. Mulliken populations (in percent) for antibonding $e_g$ (first row) and $t_{2g}$ (second row) levels of ruby derived from the present calculations for the $^4 A_2(t_{2g}^6)$ ground state of a CrO$_6^{2-}$ complex at the experimental equilibrium geometry. Results obtained for the isolated CrO$_6^{2-}$ complex are compared with those derived taking into account the internal field $E_g(r)$. Only the electronic charge lying on the 3d orbitals of chromium as well as that on 2p and 2s orbitals of three O$_1$ and three O$_2$ ligand ions is given. Due to the $C_3$ symmetry, the values given in this table mean an average value of three orbitals emerging from $t_{2g}$ under strict cubic symmetry. Note that in $^4 A_2(t_{2g}^6)$ ground state the antibonding $e_g$ levels are unoccupied while they are partially occupied in the excited $^2 T_2(t_{2g}^{2}e_g^4)$ state placed an energy 10Dq above the ground state.$^{24}$

<table>
<thead>
<tr>
<th></th>
<th>Cr(3d)</th>
<th>2p(O$_1$)</th>
<th>2p(O$_2$)</th>
<th>2s(O$_1$)</th>
<th>2s(O$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated CrO$_6^{2-}$</td>
<td>77.62</td>
<td>11.00</td>
<td>8.32</td>
<td>1.12</td>
<td>1.44</td>
</tr>
<tr>
<td>$E_g(r)$</td>
<td>86.00</td>
<td>4.61</td>
<td>7.86</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>With $E_g(r)$</td>
<td>76.06</td>
<td>10.41</td>
<td>11.82</td>
<td>0.83</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>89.40</td>
<td>3.15</td>
<td>6.05</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

the experimental value reported by Gaudry et al.$^{13}$ and is thus essentially coincident with the average Cr$^{3+}$-$O^{2-}$ distance determined for ruby (Table II).

2. Influence of the internal electric field in emerald

The form of $(-e)\Delta E_g(r)$ energy for some particular directions in emerald is depicted in Fig. 5, where $d_1$, $d_2$, $d_3$, and $d_4$ directions correspond, respectively, to a O-Cr-O path joining two opposite oxygens, a $C_2$ axis joining Cr$^{3+}$ with a close Be$^{2+}$, and the $C_3$ axis and a path bisecting a O-Cr-O angle involving two adjacent oxygen ions which does not intersect a close Be$^{2+}$ ion (Fig. 4). As it can be seen in Fig. 5, there is no electric field at the chromium site, a result consistent with the $D_3$ symmetry for emerald. Similarly to the case of ruby, $(-e)\Delta E_g(0) \approx -54$ eV. Nevertheless, the values of $(-e)\Delta E_g(r)$ for $|r| \leq 2$ Å are, in general, smaller than those found for ruby (Fig. 2), although $(-e)V_g(r) \approx -70$ eV when we move along the $d_2$ direction approaching the Be$^{2+}$ ion.

The influence of $V_g(r)$ upon the 10Dq value in emerald is shown in Fig. 3 where it is compared to the results found for ruby. In can be noticed that, in the absence of the electrostatic potential due to the rest of the lattice ions on the CrO$_6^{2-}$ complex, 10Dq would be the same for ruby and emerald. However, the changes in 10Dq due to $V_g(r)$ are very different in both gemstones, as shown in Fig. 3. The influence of internal electric field $E_g(r)$ induces a decrease of 56.413 eV and 56.357 eV on the energy of antibonding $e_g$ and $t_{2g}$ levels, respectively. Therefore, this implies only a tiny reduction of 0.05 eV on the 10Dq value calculated for the CrO$_6^{2-}$ complex $in$ $vacuo$ and thus a final 10Dq value equal to 1.95 eV. This value can be compared with the experimental figure for emerald, 10Dq = 2.00 eV.$^{3,6}$

We have also verified that the changes of electronic density induced by the internal electric field are certainly smaller for emerald than for ruby. For instance, the average 3d(Cr) population for the three $t_{2g}$ levels is found to vary by 0.15% due to the addition of the internal electric field.

V. STUDY OF A MODEL SYSTEM WITH CUBIC SYMMETRY

A. Description of the model

A central question in this study is to determine the influence of electronic density changes induced by $E_g(r)$ on the final 10Dq value. This relevant matter has been explored in the model system described in Fig. 6. In that system an octahedral

![FIG. 4. (Color online) Local structure of beryl (Be$_3$Si$_6$Al$_2$O$_{18}$) around an Al$^{3+}$ ion with a $D_3$ symmetry. All nearest O$^{2-}$ anions lie at the same distance $R = 1.903$ Å.](Image 4)

TABLE IV. Structural parameters (all in angstrom) of pure beryl (Be$_3$Si$_6$Al$_2$O$_{18}$) derived from the present periodic calculations. Aside from the lattice parameters $a$ and $c$, the distances between an Al$^{3+}$ ion and its nearest O$^{2-}$, Be$^{2+}$, and Si$^{4+}$ ions are reported. These values are compared to experimental figures derived by Gibbs et al.$^{37}$ as well as to the values of Al-O, Al-Be, and Al-Si distances obtained by Gaudry et al.$^{13}$ through periodic Carr-Parinello calculations.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Gaudry et al.</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-O</td>
<td>1.968</td>
<td>1.99</td>
<td>1.97 ± 0.005</td>
</tr>
<tr>
<td>Cr-Be</td>
<td>2.695</td>
<td>2.70</td>
<td>–</td>
</tr>
<tr>
<td>Cr-Si</td>
<td>3.306</td>
<td>3.31</td>
<td>–</td>
</tr>
</tbody>
</table>

TABLE V. Values of Al-O, Al-Be, and Al-Si distances (all in angstroms) derived from the present periodic calculations for emerald (Be$_3$Si$_6$Al$_2$O$_{18}$,$Cr^{3+}$) and those previously obtained by Gaudry et al.$^{13}$ by means of periodic Carr-Parinello calculations. The value of the Cr-O distance measured by EXAFS (Ref. 13) is also included for comparison.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Gaudry et al.</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-O</td>
<td>1.968</td>
<td>1.99</td>
<td>1.97 ± 0.005</td>
</tr>
<tr>
<td>Cr-Be</td>
<td>2.695</td>
<td>2.70</td>
<td>–</td>
</tr>
<tr>
<td>Cr-Si</td>
<td>3.306</td>
<td>3.31</td>
<td>–</td>
</tr>
</tbody>
</table>
The \( \text{CrO}_6^{9-} \) complex is surrounded by six identical point charges at the same distance \( R_q \) from the chromium ion and placed along the three \( C_4 \) axes of the octahedron. In this model system such point charges create the internal electric field on the \( \text{CrO}_6^{9-} \) unit but the octahedral symmetry is preserved. Particular attention has been paid to explore the variation of 10Dq as a function of the charge \( Q \) of the central cation and on ligands, respectively. In the case of the antibonding \( t_{2g} \) orbital, symmetry allows an admixture with valence 2p\(_x\) and 2s orbitals if the ligands are oxygens.

Although upon the addition of \( V_g(r) \) the octahedral symmetry is kept, it modifies, however, the form of orbitals and its associated energy. Therefore the energy of a given orbital \( \epsilon_n \) can be written as

\[
\epsilon_n = \epsilon_n^0 + \epsilon_n^1 + \epsilon_n^2 + \cdots, \tag{1}
\]

\[
\epsilon_n^1 = \langle \phi_n^0 | (eV_g) | \phi_n^0 \rangle, \quad \epsilon_n^2 = \sum_{\nu \neq \alpha} | \langle \phi_n^0 | (eV_g) | \phi_\nu^0 \rangle |^2 \epsilon_\nu^0 - \epsilon_n^0. \tag{2}
\]

Here \( \phi_n^0 \) and \( \epsilon_n^0 \) mean the wave function and energy, respectively, corresponding to the \( n \) orbital of the complex in the absence of the internal electric field. It is worth noting now that if \( V_g(r) \) depends linearly on \( Q \), then according to Eqs. (1) and (2), \( \epsilon_n^1 \) and \( \epsilon_n^2 \) scale like \( Q \) and \( Q^2 \), respectively.

Similarly to what is written in Eq. (1), the changes in 10Dq due to \( V_g(r) \) can shortly be written as

\[
10\Delta Dq(Q) = 10\Delta Dq(0) + \Delta_1 + \Delta_2 + \cdots, \tag{3}
\]

where 10Dq\((0)\) corresponds to the isolated complex, while \( \Delta_1 \) and \( \Delta_2 \) depend on \( Q \) and \( Q^2 \), respectively. It should be noticed now that \( \Delta_1 \) reflects the 10Dq variation in first-order perturbation, which is derived using the frozen wave functions corresponding to \( V_g(r) = 0 \). By contrast, the correction called \( \Delta_2 \) does reflect the change of electronic density induced by the internal electric field.

In an isolated transition metal complex the antibonding \( t_{2g} \) and \( e_g \) levels have the form:

\[
|t_{2g}; r\rangle = \alpha_t |d(t_{2g}); r\rangle - \beta_{p\sigma} |\chi_{p\sigma}; r\rangle \quad (r = xy, xz, yz) \tag{4}
\]

\[
|e_g; r\rangle = \alpha_e |d(e_g); r\rangle - \beta_{p\sigma} |\chi_{p\sigma}; r\rangle - \beta_s |\chi_s; r\rangle \quad (r = x^2 - y^2, 3z^2 - r^2). \tag{5}
\]

In Eq. (4) the first term on the right describes a pure d wave function transforming like \( xy, xz, \) or \( yz \), while the second term means a suitable linear combination of atomic orbitals (LCAO) involving \( p_x \) valence orbitals of six ligands. The coefficients \( \alpha_t \) and \( \beta_{p\sigma} \) thus reflect the probability of finding the electron on the central cation and on ligands, respectively. In the case of the antibonding \( e_g \) orbital, symmetry allows an admixture with valence \( 2p_x \) and \( 2s \) orbitals if the ligands are oxygens.

Let us know see what the changes of both \( t_{2g} \) and \( e_g \) levels due to the addition of an internal field which keeps the cubic symmetry are. According to Eq. (2), if \( V_g(r) \) also exhibits cubic symmetry, such orbitals can be mixed only with orbitals of the same label. So, the antibonding \( t_{2g} \) level can be mixed with the bonding counterpart called \( t_{2g}^{e}\), giving rise to changes in \( \beta_{p\sigma} \). Similarly, the antibonding \( e_g \) level for the isolated complex mixes with the mainly \( 2p_x \) level called \( e_g^{p\sigma} \), as well as with the mainly \( 2s \) level denoted as \( e_g^{s} \). This admixture leads to changes of \( \beta_{p\sigma} \) and \( \beta_s \) quantities when a nonconstant \( V_g(r) \) potential on the complex is switched on.

Let us denote by \( \beta_{p\sigma}(E), \beta_s(E) \), or \( \beta_{p\sigma}(E) \) the molecular orbital coefficients associated with a given \( E_g(r) \). Obviously, if there is no electric field \( \beta_{p\sigma}(0) \equiv \beta_{p\sigma}, \beta_s(0) \equiv \beta_s \) and \( \beta_{p\sigma}(0) \equiv \beta_{p\sigma} \). Using second-order perturbation theory, the expression for \( \Delta_2 \) turns out to be

\[
\Delta_2 = [\beta_{p\sigma}(E) - \beta_{p\sigma}(0)]^2 [\epsilon(e_g) - \epsilon(e_g^p)]
\]

\[
+ [\beta_s(E) - \beta_s(0)]^2 [\epsilon(e_g) - \epsilon(e_g^s)]
\]

\[
+ [\beta_{p\sigma}(E) - \beta_{p\sigma}(0)]^2 [\epsilon(t_{2g}) - \epsilon(t_{2g}^p)], \tag{6}
\]
where \( \varepsilon(e_g) \), \( \varepsilon(t_{2g}) \), \( \varepsilon(e'_{g}) \), or \( \varepsilon(t_{2g}') \) stand for orbital energies of the isolated complex. This expression allows one to estimate the value of \( \Delta_2 \) associated with a given internal field from the values of \( \beta_{p\sigma}(E) \), \( \beta_s(E) \), or \( \beta_{p\pi}(E) \) and the orbital energies of the isolated complex derived from \textit{ab initio} calculations.

### B. Results on the model system

Calculated values of 10Dq as a function of the external charge \( Q \) are portrayed in Fig. 7 where \( Q \) is varied in the range between \(-2e\) and \(5e\). It can be noticed that the dependence of the calculated 10Dq upon \( Q \) is essentially linear. Bearing in mind that the contributions \( \Delta_1 \) and \( \Delta_2 \) in Eq. (3) scale like \( Q \) and \( Q^2 \), respectively, the results displayed in Fig. 7 already suggest that the changes in electronic density play a minor role for understanding the variations undergone by 10Dq due to the presence of the internal field. In other words, the changes are primarily due to first-order effects [reflected in Eq. (2)], thus involving only the \textit{frozen} wave functions of the isolated complex.

Seeking to reinforce this view, we have estimated the \( \Delta_2 \) contribution by means of Eq. (6) and the values of \( \beta_{p\sigma}(E) \), \( \beta_s(E) \), or \( \beta_{p\pi}(E) \) and the involved excitations derived from the present calculations. In Table VI the values of 10Dq and the \( \beta_{p\sigma}(E) \), \( \beta_s(E) \), or \( \beta_{p\pi}(E) \) parameters calculated for \( Q = 3e \) are compared to those for the complex in \textit{vacuo} (\( Q = 0 \)). For estimating the second-order contribution \( \Delta_2 \), we have used the values \( \varepsilon(e_g) - \varepsilon(e'_{g}) = 8.2 \text{ eV} \), \( \varepsilon(t_{2g}) - \varepsilon(t_{2g}') = 6.4 \text{ eV} \), and \( \varepsilon(e_g) - \varepsilon(e'_{g}) = 21 \text{ eV} \) derived from the present calculations for \( Q = 0 \).

It can be remarked in Table VI that on passing from the complex in \textit{vacuo} to \( Q = 3e \), the value of 10Dq decreases by 0.6 \text{ eV}, while \( \Delta_2 \) is estimated to be one order of magnitude lower. Bearing in mind that 10Dq(\( Q = 10Dq(0) \)) for \( Q = 3e \) is four times bigger in the model system than for ruby, it is thus reasonable to accept that in all these cases the changes in 10Dq are governed by the \( \Delta_1 \) contribution where only the \textit{frozen} wave functions of the isolated complex are involved.

On Fig. 8 the form of \((-e)V_{R}(r)\) along \(\{100\}\) and \(\{110\}\) directions is depicted. It can be noted that, as expected, when \( r \) is parallel to \(\{100\}\) then \((-e)V_{R}(r) < (-e)V_{R}(0)\) and thus the electrons which are close to ligands experience a \textit{supplementary} electrostatic attraction. Let us now consider an \( e_g \) level where the electronic charge is lying mainly along \(\{100\}\) directions. Therefore, if we designate by \( \langle e_g \rangle \) the wave function of such a level for \( Q = 0 \), then, according to Fig. 8 the quantity \( \langle e_g \rangle |(-e)V_{R}\langle e_g \rangle| \) tends to decrease the energy of the \( e_g \) level. On the contrary, \((-e)V_{R}(r)\) along \(\{110\}\) directions increases slightly when \(|r|\) does. This result is consistent with the form of an electrostatic potential \( V_{R}(r) \) in cubic symmetry:

\[
V_{R}(r) = A(x^4 + y^4 + z^4 - \frac{1}{2} r^4) + \cdots \quad (7)
\]

As in the \( t_{2g} \) level, if the wave functions are pointing at \(\{110\}\) directions, then the quantity \( \langle t_{2g}' \rangle |(-e)V_{R}\langle t_{2g}' \rangle| \) increases the energy of such a level. Therefore, in accordance with this reasoning, the electric field reflected in Fig. 8 tends to reduce the 10Dq value. This explains, albeit qualitatively, the results displayed in Table VI.

It is worth noting now that the addition of \( V_{R}(r) \) increases the value of \( \alpha_x^2 \) corresponding to the antibonding \( e_g \) level.
(Table VI), while the opposite happens for the fully occupied e_g^2 level. This gives rise again to a net flow of the electronic charge from central ion to ligands consistent with the form of (−e)V_b(r) along the (100) directions depicted in Fig. 8.

Following the present analysis, if we rotate the four Q charges lying in the XY plane by an angle θ = 45° it can be expected that this new potential decreases the energy of the xy orbital while increasing that corresponding to the \( x^2−y^2 \) orbital. Despite that this new potential has a tetragonal symmetry, we have verified that it increases the separation between \( x^2−y^2 \) and \( e_g^2 \) orbitals and the 10Dq value.

C. Application to gemstones

The analysis carried out in the foregoing section strongly supports that the change in 10Dq in ruby is essentially related neither to the polarization of the chromium ion nor to the polarization change on ligands induced by the internal electric field. In fact, both phenomena do involve a change of electronic density, while we have shown that these effects play a secondary role for understanding the changes due to \( E_p(r) \).

The present analysis points out that the changes in 10Dq arise from the different form of \( V_b(r) \) along different directions keeping the electronic density of the isolated complex. In the case of ruby the form of \( V_b(r) \) along \( d_2 \) and \( d_3 \) directions (Fig. 2) is not symmetric around \( r = 0 \), and \( (−e)[V_b(r)−V_b(0)] < 0 \) when we approach a close aluminum ion. Bearing in mind that \( t_{2g} \) orbitals are lying mainly along such directions, the action of \( (−e)V_b(r) \) tends to decrease the energy of such orbitals. By contrast, the variation of \( V_b(r) \) along metal-ligand directions is more symmetric and much softer than for \( d_2 \) and \( d_3 \) directions. Therefore, it can reasonably be expected that \( V_b(r) \) induces a bigger decrease for \( t_{2g} \) orbitals than for \( e_g \) ones lying along metal-ligand directions. This explains albeit qualitatively the increase of 10Dq due to the internal field in the case of ruby (Fig. 3).

In the case of emerald (Fig. 5), the quantity \( |V_b(r)−V_b(0)| \) is in general smaller than that obtained for ruby. Nevertheless, it is comparable to that found for the model system (Fig. 8). Despite this fact the internal field only produces a little variation on 10Dq in the case of emerald. If we look at \( d_2 \), \( d_4 \), and \( d_4 \) directions where \( t_{2g} \) orbitals are lying, we see that the effect of \( V_b(r) \) is not homogeneous. For instance, it tends to raise the orbital energy for \( d_4 \) and \( d_4 \) directions while when the electron approaches a close Be^{2+} such energy decreases. This suggests the existence of a compensation mechanism behind the actual 10Dq value for emerald.

For clarifying this matter we have calculated the 10Dq value of the emerald including in \( V_b(r) \) only the electrostatic potential coming from the nearest Be^{2+} ions. In a second step we have also included in the calculation the electrostatic potential arising from the six nearest Si^{4+} ions. These results, gathered in Table VII, are compared to those obtained including in \( V_b(r) \) all ions lying outside the CrO_6\(^{2−}\) complex. It can be noticed that if only the nearest Be^{2+} ions are considered when calculating \( V_b(r) \), it leads to 10Dq = 2.20 eV, which is 10% higher than the value obtained for the isolated CrO_6\(^{2−}\) unit at \( R = 1.97 \) Å. By contrast, when the next shell involving six Si^{4+} ions at 3.31 Å from Cr^{3+} is also taken into account, then the value 10Dq = 1.93 eV is practically coincident with the figure 10Dq = 1.95 eV obtained including in \( V_b(r) \) all ions lying outside the CrO_6\(^{2−}\) complex. On one hand, this fact stresses that the quantity \( V_b(r)−V_b(0) \) governing 10Dq mainly depends on the first shells around the complex. In other words, although all ions are contributing to \( V_b(0) \), nevertheless \( V_b(r)−V_b(0) \) and \( Δ_1 \) are essentially reproduced considering only a few shells of ions around the complex.\(^{32,60} \) On the other hand, it proves that the very small changes induced by \( V_b(r) \) on the 10Dq value in emerald is the result of a practical cancellation of the contribution due to the three Be^{2+} ions at 2.66 Å by that coming from six Si^{4+} ions at 3.31 Å. This finding has some similarities with the near independence of 10Dq upon \( V_b(r) \) in the case of perovskites like K\( \text{MgF}_2 \) doped with \( \text{Mn}^{2+} \) or \( \text{Ni}^{2+} \).\(^{32,60} \) In such a case this behavior comes from the cancellation of the contribution to 10Dq due to the first shell of eight K^{+} ions by that of the second shell involving six Mg^{2+} ions. By contrast, a different situation holds for the inverse perovskite Li\( \text{BaF}_3 \) doped with divalent impurities where \( Δ_1 \) arises mainly from the first shell made by eight Ba^{2+} ions.\(^{32} \)

VI. FINAL REMARKS

The present results stress the relevance of internal fields for a good understanding of optical and magnetic properties of transition-metal impurities in insulators. This situation thus has some connections with the interpretation of the quadrupole splitting on a given nucleus placed in a noncubic site, observed either in Mossbauer spectroscopy\(^{61} \) or through magnetic resonance techniques.\(^{62} \) Indeed, a right understanding of such splitting requires calculation of the quantities \( ⟨\frac{∂^2V}{∂x_i^2}⟩_0 \) at the nucleus site \( (x_i = 0) \), where \( V(x_i) \) just means the electrostatic potential around the nucleus due to the rest of nuclei and the electronic charge.\(^{63} \)

The results and analysis carried out in this work confirm that the different color exhibited by Cr\(^{3+} \) gemstones is due neither to differences in the mean Cr\(^{3+}−O^{2−} \) distance nor to the flow of unpaired electrons outside the CrO_6\(^{2−} \) unit. By contrast, the small changes in 10Dq and the color shift in the series of ionic oxides doped with Cr\(^{3+} \) can reasonably be understood considering only the CrO_6\(^{2−} \) unit and the internal field \( E_p(r) \) created by the rest of lattice ions upon the localized electrons. This result thus concurs with a previous study showing that the separation \( Δ(2T_1;^4T_2) \) between \( ^2T_2(e_g^2;e_g^2) \) and \( ^4T_1(e_g^2;e_g^2) \)
states as well as the energy $E(2E)$ of the $^2E(t_{2g}^5) \rightarrow ^4A_2(t_{2g}^3)$ emission transition of Cr$^{3+}$ in different lattices can be well accounted for on the same grounds.\textsuperscript{34}

As a salient feature the present study demonstrates quantitatively that the modifications of electronic density due to the internal field do not play a relevant role for understanding the changes induced on the tetragonal geometry and the involved Jahn-Teller energy, $E_{JT}$, can also be understood only through the frozen wave functions corresponding to the initial high-symmetry configuration. By contrast, the barrier among equivalent distorted configurations partially depends on the electronic density change induced by the distortion.\textsuperscript{65}

Despite the fact that all ions outside the CrO$_6$– unit contribute to the electrostatic potential at the chromium site $V_R(0)$, it has been emphasized through this work that the variations on 10Dq come from the quantity $V_R(r) - V_R(0)$, which is essentially reproduced through the first shells of ions around the complex. A similar conclusion was reached in a previous study on the color shift along the series of Al$^{2-}$, Cr$_3$O$_3$ mixed crystals.\textsuperscript{60}

Bearing in mind the present study, it is tempting to try to explain why the 10Dq value measured for MgO:Cr$^{3+}$ (Ref. 66) is coincident with that of emerald. As the Mg$^{2+}$O$^{2-}$ distance in MgO is 2.10 Å, it is hard to accept that the Cr$^{3+}$O$^{2-}$ distance in MgO:Cr$^{3+}$ is the same as in emerald. Work along this line is now underway.

ACKNOWLEDGMENTS

Support from the Spanish Ministerio de Ciencia y Tecnología under Project No. FIS2009-07083 is acknowledged.

\begin{thebibliography}{99}
\end{thebibliography}
48. CRYSTAL basis sets, http://www.crystal.unito.it/Basis_Sets/Ptable.html.