4f and 5d levels of Ce$^{3+}$ in $D_2$ eightfold oxygen coordination

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The effects of the first coordination shell geometry of the trivalent Cerium ion (Ce$^{3+}$) on its 4f and 5d levels in Ce-doped oxides with a $D_2$ 8-fold site, like garnets, are studied with embedded cluster, wave function based ab initio methods. The only deformations of a $D_2$ CeO$_8$ moiety that are found to shift the lowest 4f $→$ 5d transition to the red (longer wavelengths) are the symmetric Ce-O bond compression and the tetragonal symmetric bond bending. In a first approximation, the lowest 5d level of Ce$^{3+}$ in garnets can be understood as resulting from the cubic $E_g$ level with a strong $E_g$ $×$ $e_g$ Jahn-Teller coupling. These results are analyzed in terms of 5d $→$ 4f centroid energy differences and ligand field stabilizations. The splittings of the upper 5d levels and of the 4f levels are also discussed.

Keywords: Cerium, Ce$^{3+}$, 4f, 5d, $D_2$, oxides, garnets, 8-fold coordination

I. INTRODUCTION

Yttrium aluminum garnet Y$_3$Al$_5$O$_{12}$ (YAG) doped with Ce$^{3+}$ is a well known phosphor with a blue Ce$^{3+}$ 4f $→$ 5d absorption and a corresponding yellow 5d $→$ 4f emission, which is used in InGaN blue LED based, white light solid-state lighting devices. In the search for alternative phosphors with the best efficiencies and tailored color-rendering indexes, doping Ce$^{3+}$ in other artificial garnets has been a line of work. It led, for instance, to the discoveries of the Lu$_2$CaMg$_{5/2}$Si$_{3/2}$O$_{12}$:Ce$^{3+}$ orange phosphor and the Ca$_3$Sc$_2$Si$_3$O$_{12}$:Ce$^{3+}$ green phosphor.

Most garnets can be described in terms of a 160 atom body-centered cubic unit cell (80 atom primitive cell) of the $Ia3d$ (230) space group, which contains eight formula units of $A_3B'_4B''_4O_{12}$. A, B’ and B” are cations of different nominal charges in different symmetry sites. In Y$_3$Al$_5$O$_{12}$, for instance, $A$=Y, $B’$=Al, and $B”$=Al, all with oxidation states +3. In Ca$_3$Sc$_2$Si$_3$O$_{12}$, $A$=Ca, $B’$=Sc, and $B”$=Si, with respective oxidation states +2, +3, and +4. In Lu$_2$CaMg$_{5/2}$Si$_{3/2}$O$_{12}$, 2/3 of the A sites are occupied by Lu and 1/3 by Ca atoms. $B’$=Mg, and $B”$=Si, with respective oxidation states +3, +2, +2 and +4. In all cases, A occupy 24(c) sites of 8-fold coordination, $B’$ 16(a) sites of 6-fold coordination, and $B”$ 24(d) sites of 4-fold coordination, all of them at fixed positions, with the remaining 96 O atoms in (h) sites, which depend on three $x$, $y$ and $z$ internal parameters. Optically active Ce$^{3+}$ impurities substitute for A atoms at (c) sites, which have the local symmetry of the $D_2$ point group and a first coordination shell made of 8 oxygen atoms.

The energies of the 4f and 5d levels of Ce$^{3+}$ in particular garnets and in other oxides depend on the bonding and electrostatic interactions between Ce and the hosts, and they can be calculated in a one-by-one basis, with reasonable accuracy, by means of ab initio methods, both in $D_2$ local symmetry like in Ce-doped YAG and in lower local symmetries like in Ce,La-doped YAG and Ce,Ga-doped YAG. These energies are dominated, up to first-order, by the bonding interactions between Ce and its first oxygen coordination shell, subject to the basic confinement embedding effects of the host. Other specific host embedding effects are important at higher orders of approximation and they refine the results.

This paper is aimed at providing a basic study of the energies of the levels of the 4f$^1$ and 5d$^1$ manifolds of Ce$^{3+}$ in $D_2$ 8-fold oxygen coordination. We report the results of an ab initio calculation of them after consideration of the bonding interactions with the first oxygen coordination shell only, under the effects of a cubic, non host specific, confinement embedding potential. The present results are a common reference for the 4f and 5d levels of Ce$^{3+}$ in specific garnets (and other oxides with 8-fold coordination), which can be considered as resulting from them after including the host specific embedding effects.

II. METHOD

In order to know the 4f and 5d energy levels of Ce$^{3+}$ under the effects of its interactions with a coordination shell of eight oxygens in a $D_2$ symmetry site of a solid oxide, we calculated the corresponding energy levels of the (CeO$_8$)$_{3/2}$ cluster embedded in a $O_h$ host potential. We will describe later the details of the ab initio wave function based quantum mechanical calculation. With the choice of a host embedding potential of cubic symmetry, all the energy splittings and changes due to $D_2$ distortions are ascribable to the interactions between Ce and the O atoms.

It is convenient to look at the $D_2$ energy levels as derived from the more familiar $O_h$ levels after geometry distortions and this is what we did in this work. In consequence with this, we decided to take a cubic CeO$_8$ $O_h$ moiety as a reference and to chose six atomic displacement coordinates $S_1 - S_6$ that transform according to irreducible representations of the $O_h$ point symmetry group for the six degrees of freedom of the CeO$_8$ $D_2$ moiety. They are defined in Table I and represented in Fig. 1; more details are given in the Appendix. $S_1$ represents the breathing (or symmetric bond stretching) of the reference cube and it transforms accord-
ing to the totally symmetric irreducible representation $a_{1g}$; 
$\delta_2$ represents an asymmetric bond stretching of the crosses 
$a_1 - a_2 - a_3 - a_4$ and $e_1 - e_2 - e_3 - e_4$ and it transforms 
according to the $e_g$ sub-species of the doubly degenerate 
$e_g$ irreducible representation;\textsuperscript{11} $S_3$ and $S_4$ are the symmetric 
$(e_g, \theta)$ and asymmetric $(e_g, e)$ bond bendings of the $a$ and 
e; crosses; finally, $S_5$ and $S_6$ are the symmetric $(e_e, \theta)$ and 
asymmetric $(e_e, e)$ twistings of the crosses.

The details of the quantum mechanical calculation are 
the following. We performed \textit{ab initio} calculations on a 
(CeO\textsubscript{8})\textsuperscript{13−} cluster which include Ce-O bonding effects, 
static and dynamic electron correlation effects, scalar and 
spin-orbit coupling relativistic effects, and cubic host em-
bedding effects. For each $D_2$ nuclear configuration of the 
(CeO\textsubscript{8})\textsuperscript{13−} embedded cluster, we performed, in a 
first step, scalar relativistic calculations with the many-
electron second-order Douglas-Kroll-Hess (DKH) Hamilto-
nian.\textsuperscript{12,13} These were state-average complete-active-space 
self-consistent-field\textsuperscript{14–16} (SA-CASSCF) calculations with the 
active space that results from distributing the open-shell 
electron in 13 active molecular orbitals with main char-
acter Ce 4$f$, 5$d$, 6$s$, which provided occupied and empty 
molecular orbitals to feed subsequent multi-state second-
order perturbation theory calculations (MS-CASPT2).\textsuperscript{17–20} 
where the dynamic correlation of 73 electrons (the 
5$s$, 5$p$, 4$f$, 5$d$, 6$s$ electrons of Ce and 2$s$, 2$p$ electrons of the 
O atoms) were taken into account. In a second step, spin-
orbit coupling effects were included by adding the AMFI 
approximation of the DKH spin-orbit coupling operator\textsuperscript{21} 
to the Hamiltonian and performing restricted-active-space 
state-interaction spin-orbit calculations (RASSI-SO)\textsuperscript{22} with 
the previously computed SA-CASSCF wave functions and 
MS-CASPT2 energies. All are all-electron calculations with 
atomic natural orbital (ANO) relativistic basis sets for Cerium\textsuperscript{23} and Oxygen.\textsuperscript{24}

In all these calculations, the Hamiltonian of the 
(CeO\textsubscript{8})\textsuperscript{13−} cluster is supplemented with a cubic embedding 
Hamiltonian. For this we chose the \textit{ab initio} model potential 
embedding Hamiltonian (AIMP)\textsuperscript{25} of a SrO host in its 
high pressure CsCl lattice structure\textsuperscript{26} (Pm\textsubscript{3}m, no. 221), 
which provides a perfect 8-fold cubic oxide coordination of 
the cationic site. We used a lattice constant $a = 2.87$ Å 
(the one that gives a Ce-O equilibrium distance in the cubic 
(CeO\textsubscript{8})\textsuperscript{13−} embedded cluster of 2.34 Å at the MS-CASPT2 
level of calculation, which is the Ce-O distance of the reference 
CeO\textsubscript{8} cube in an hypothetical undistorted Ce-doped 
YAG\textsuperscript{26}). The embedding potential of this 8-fold coordinated 
cubic oxide was computed in Hartree-Fock self-consistent 
embedded-ions calculations (SCEI),\textsuperscript{27} in which the input 
embedding AIMPs used for the Sr\textsuperscript{2+} and O\textsuperscript{2−} ions of SrO 
are consistent with the output AIMPs obtained out of the 
HF orbitals of the embedded Sr\textsuperscript{2+} and O\textsuperscript{2−} ions.

III. RESULTS

The dependence of the $4f \rightarrow 4f$ and $4f \rightarrow 5d$ transi-
tions on the $D_2$ distortions of the first coordination shell 
are shown in Fig. 2 without spin-orbit coupling and in 
Fig. 3 with spin-orbit coupling interactions included. The 
chosen ranges of the $S_1 - S_8$ coordinates span their usual 
values in natural and artificial garnets, which are shown 
in Table II and in the Figures. Besides the transitions, the 
Figures include two additional lines: One is the dif-
fERENCE between the 5$d$ and 4$f$ energy centroids (aver-
gage energies of the five 5$d^1$ levels and the seven 4$f^1$ 
levels), $\Delta E_{\text{centroid}} = E_{\text{centroid}}(5d^1) - E_{\text{centroid}}(4f^1)$; the 
other is the difference between the ligand field stabiliza-
tion energies of the 5$d$ and 4$f$ lowest levels $\Delta E_{\text{ligand field}} = [E_{\text{centroid}}(5d^1) - E_1(5d^1)] - [E_{\text{centroid}}(4f^1) - E_1(4f^1)]$. (See 
Fig. 2 in Ref. 9.) The fact that the lowest 4$f \rightarrow 5d$ 
transition equals their subtraction, $E_1(5d^1) - E_1(4f^1) = 
\Delta E_{\text{centroid}} - \Delta E_{\text{ligand field}}$, has been used to analyze the rea-
sons behind red and blue shifts of this transition.\textsuperscript{9,10}

Let us first focus on the lowest 4$f \rightarrow 5d$ transition, 
whose reverse is the luminescence of Ce\textsuperscript{3+} in 
garnets and other oxides. It is clear that only two coordinates have 
an important impact on it: the breathing mode $S_1$, which does 
not distort the cubic symmetry, and the symmetric bond 
bending mode $S_3$, which gives a $e_g$ tetragonal distortion of the 
CeO\textsubscript{8} cube.

Symmetric compression of the Ce-O bonds lowers the 
4$f \rightarrow 5d$ transition. This is almost entirely due to the 
increase of the 5$d$ ligand field it produces, which lowers 
the first 5$d^1$ level with respect to its centroid. This effect 
is slightly compensated with a small increase due to the 
centroids: bond compression slightly shifts the 5$d$ centroid 
upwards with respect to the 4$f$ centroid. The latter ob-
ervation has been made before\textsuperscript{10,28} and it contradicts the 
predictions of the usual model for the centroid energy dif-
fERENCE,\textsuperscript{29–31} according to which it should be smaller for 
smaller bond lengths; nevertheless, the model has been 
useful to rationalize 5$d \rightarrow 4f$ luminescences.\textsuperscript{32} The con-
tribution of the breathing mode $S_1$ to the shift of the lower-
est 4$f \rightarrow 5d$ transition energy represented in Fig. 3 fits 
8255 $S_1 - 4803 S_1$ (S in Å, energy shift in cm$^{-1}$); for cubi 
CeO\textsubscript{8} moieties $S_1 = 2\sqrt{2}\Delta d$, $\Delta d$ being the Ce-O bond 
length change with respect to the reference cube; in our 
case the reference cube has Ce-O bond length of 2.34 Å 
and a lowest 4$f \rightarrow 5d$ transition of 2600 cm$^{-1}$.

Symmetric bond bending along the $S_3$ coordinate lowers 
de 4$f \rightarrow 5d$ transition. Among the $D_2$ distortions of the 
cube, it is the only tetragonal one. Also, it is the only one 
with a significant impact on the transition (for the ranges 
of $S_2 - S_8$ shown by garnets). The enhancement of tetra-
goonal distortions of the cube as responsible for the red-shifts 
of the Ce\textsuperscript{3+} luminescence has been suggested by Chetham 
and coworkers\textsuperscript{33} and it is supported by the present inves-
tigation. The image emerging from an analysis in terms of 
configuration energy centroids and ligand field stabiliza-
tion is one in which the lowering of the first 5$d^1$ level with 
respect to the ground state is due in almost equal amounts 
to an increase of the ligand field (of its tetragonal com-
ponent) and to a reduction of the centroid energy dif-
ference. Again, the latter effect contradicts the prediction of
the Judd-Morrison model: a very small increase of the centroid energy difference out of a very small increase of the Ce-O distances. The contribution of the tetragonal mode $S_1$ (in Å) to the shift of the lowest $4f \rightarrow 5d$ transition (in cm$^{-1}$) represented in Fig. 3 fits $1844S_3 - 2885S_3^2$ for $S_3 < 0$ and $-1876S_3 - 141S_3^2$ for $S_3 > 0$. This contribution is due in almost equal amounts to the lowering of the centroid energy difference and the increasing of the ligand field. The centroid effect fits $10S_3 - 2695S_3^2$ for $S_3 < 0$ and $12S_3 - 2581S_3^2$ for $S_3 > 0$; the ligand field effect fits $1834S_3 - 190S_3^2$ for $S_3 < 0$ and $-1887S_3 + 2440S_3^2$ for $S_3 > 0$.

Apart from $S_1$ and $S_3$, only the asymmetric stretching $S_2$ has an effect on the first $4f \rightarrow 5d$ transition, although it is a very small one (it fits $-2033S_2^2$ in the range of the figures). This result allows one to say that, in a first approximation and in spite of the large values of the $S_i$ coordinates applicable to garnets, the lowest 5d level can be understood as resulting from the cubic $E_g$ level with a strong $E_g \times e_g$ Jahn-Teller coupling.44

Regarding higher $4f \rightarrow 5d$ transitions, several remarks can be made from Figs. 2 and 3. The splitting of the first and second 5d levels related with the cubic $2E_g$ is due to the symmetric bending $S_3$ and to the symmetric twisting $S_5$, with a significantly higher contribution from the latter in garnets; however, different splittings in different garnets would be due to $S_3$. The splittings of the three upper levels, mostly related with the cubic $2T_{2g}$, come basically from the symmetric bending $S_3$ and the asymmetric stretching $S_2$, with a small contribution from the symmetric twisting $S_5$ and negligible contributions from the asymmetric bending and twisting $S_4$ and $S_6$. The larger $S_1$ and the absolute values of $S_2$ and $S_3$, the higher probability for the third 5d level to appear below the conduction band of the garnet.

Finally, the $4f$ levels are shown in more detail in Figs. 4 and 5, without and with spin-orbit coupling respectively. These are interesting because the 5d $\rightarrow$ 4f emission is made of the superposition of the seven individual emissions and the full width and shape of the emission band depends on the relative positions of the 4f levels, although not only on them. Since the emission to the highest 4f level ($7T_{5}^\circ$ or $4f_7$) has a minor contribution to the full emission band shape, we can have a predictive hint by looking at the six lowest 4f levels. (Note that the experimental 5d $\rightarrow$ 4f emission exhibits two peaks or shoulders, which are often taken as the difference between the $2F_{7/2}$ and $2F_{5/2}$ in the garnets; this difference is around 2000 cm$^{-1}$ in Fig.5.) According to Fig. 5, the emission band width seems to be controlled by $S_2$ and $S_3$, so that the garnets with higher absolute values of these two coordinates would tend to have wider emission bands because of their higher 4f level separation. Of course, the width of each individual 5d $\rightarrow$ 4f emission will depend on the 5d and 4f equilibrium offsets.

Since only the first coordination shell effects in a hypothetical undistorted Ce$_A$ substitutional defect are properly taken into account in this work, whereas the host specific electronic effects and the structural relaxation effects after the substitution are disregarded, direct comparisons of the present results with experiments must be taken with care. Nevertheless, it is interesting to see how these results compare with experiments in the most studied case of Ce$^{3+}$-doped YAG: It gives us a hint on the size of the disregarded contributions. The results are summarized in Table III. The host specific embedding and structural relaxation effects are not large but are significant. Different signs and sizes are observed in different states, which are a consequence of effects on the effective field of the second and more distant neighbors, as well as of local (mostly first neighbor) relaxations. These additional effects on the effective ligand field are shown, for instance, in the different impacts on the total splitting of the 5d shell (30150 vs. 33200 cm$^{-1}$, -10%), on the splitting of the four first 5d levels (28500 vs. 27880 cm$^{-1}$, +2%; with 26900 cm$^{-1}$ experimental), and on the splitting of the two first 5d levels (7620 vs. 4000 cm$^{-1}$, +48%; with 7400 cm$^{-1}$ experimental). The only consideration of the first coordination shell of Cr$^{3+}$ gives a good qualitative and even semi-quantitative description of the four 5d levels of Ce$^{3+}$ in YAG that have been experimentally observed, which are quite reasonably reproduced by the ab initio calculations in Ref. 8.

IV. CONCLUSIONS

The levels of the $4f^{1}$ and $5d^{1}$ manifolds of Ce$^{3+}$ in $D_2$-fold oxygen coordination have been calculated ab initio as a function of $D_2$ deformation coordinates of a reference cube, with the goal of pinpointing the effects of the geometry of the first coordination shell. A (CeO$_6$)$_{13-}$ cluster under the effects of a confinement AIMP embedding potential of cubic symmetry has been used at a level of calculation all-electron DHK for the Hamiltonian and SA-CASSCF/MS-CASPT2/RASSI-SO for the wave functions. The results include bonding, correlation, scalar relativistic, spin-orbit coupling, and embedding interactions.

It is found that, within the range of $D_2$ distortions covering natural and artificial garnets, the lowest 4f $\rightarrow$ 5d transition shifts significantly to the red only as a consequence of symmetric Ce-O bond compression and tetragonal symmetric bond bending. Then, in a first approximation, the lowest 5d level of Ce$^{3+}$ in garnets can be understood as resulting from the cubic $E_g$ level with a strong $E_g \times e_g$ Jahn-Teller coupling.

The increase of the 5d cubic ligand field dominates the effects of the bond compression, whereas the effect of the tetragonal bond bending distortion is divided in almost equal amounts between an increase of the 5d tetragonal ligand field and a reduction of the energy difference between the 5d and 4f energy centroids.

The splittings of the upper 5d levels and of the 4f levels have also been studied.
Acknowledgments

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APPENDIX

We have chosen Oxygen atoms $a_1$ and $e_1$ (see Table I and Fig. 1) as the symmetry independent atoms. The other atoms are obtained upon application of the $D_2$ point group symmetry operations. So, any particular $D_2$ atomic configuration of the CeO$_8$ moiety is defined with $\vec{r}_{a_1} = (x_{a_1}, y_{a_1}, z_{a_1})$, $\vec{r}_{e_1} = (x_{e_1}, y_{e_1}, z_{e_1})$, $\vec{r}_{e_2} = \vec{C}_{2y} \vec{r}_{a_1}$, $\vec{r}_{e_3} = \vec{C}_{2y} \vec{r}_{e_1}$, $\vec{r}_{e_4} = \vec{C}_{2x} \vec{r}_{a_1}$, $\vec{r}_{e_5} = \vec{C}_{2x} \vec{r}_{e_1}$.

Taking an arbitrary reference cube with Ce-O distance $d$, in which the chosen positions for $a_1$ and $e_1$ are $\vec{r}_{a_1,ref} = ((\sqrt{2},0,1)d/\sqrt{3}$ and $\vec{r}_{e_1,ref} = (0,\sqrt{2},1)d/\sqrt{3}$, the $D_2$ atomic configurations of the CeO$_8$ moiety can also be defined in terms of displacements of the symmetry independent atoms $\delta \vec{r}_{a_1} = \vec{r}_{a_1} - \vec{r}_{a_{1,ref}} = (x_{a_1} - d/\sqrt{3}, y_{a_1}, z_{a_1} - d/\sqrt{3})$ and $\delta \vec{r}_{e_1} = \vec{r}_{e_1} - \vec{r}_{e_{1,ref}} = (x_{e_1}, y_{e_1} - d/\sqrt{3}, z_{e_1} - d/\sqrt{3})$, together with the displacements of the symmetry dependent atoms $\delta \vec{r}_{e_2} = \vec{C}_{2y} \delta \vec{r}_{a_1}$, $\delta \vec{r}_{e_3} = \vec{C}_{2y} \delta \vec{r}_{e_1}$, $\delta \vec{r}_{e_4} = \vec{C}_{2x} \delta \vec{r}_{a_1}$, $\delta \vec{r}_{e_5} = \vec{C}_{2x} \delta \vec{r}_{e_1}$, $\delta \vec{r}_{e_6} = \vec{C}_{2y} \delta \vec{r}_{e_4}$, $\delta \vec{r}_{e_7} = \vec{C}_{2y} \delta \vec{r}_{e_5}$, $\delta \vec{r}_{e_8} = \vec{C}_{2x} \delta \vec{r}_{e_4}$, $\delta \vec{r}_{e_9} = \vec{C}_{2x} \delta \vec{r}_{e_5}$.

Substitution of the values of these atomic displacements in the equations in Table I gives the values of the $D_2$ totally symmetric displacement coordinates of the CeO$_8$ moiety $S_1, S_2, \ldots S_6$.

We may note that, if a cube with a different Ce-O distance was taken as a reference, all $D_2$ displacement coordinates would remain the same except for $S_1$. So, it may be convenient to chose, for a particular $D_2$ configuration, the reference cube that gives $S_1 = 0$; this particular cube has a Ce-O distance $d_{ref} = d + S_1/\sqrt{8}$. In other words, we can define any $D_2$ configuration of the CeO$_8$ moiety using $d$ and $S_1, S_2, \ldots S_6$, or, alternatively, using $d_{ref}$ and $S_1 = 0, S_2, \ldots S_6$.

Also, we should remark that, although a general $D_2$ configuration of the CeO$_8$ moiety has six degrees of freedom, the $D_2$ configurations of the original AO$_8$ moiety in undoped garnets only has four degrees of freedom. These are usually given in terms of the $Ia\overline{3}d$ space group structural parameters $a, x_O, y_O, z_O$; $a$ being the lattice constant and $x_O, y_O, z_O$ the fractional coordinates of the special position (h) occupied by the Oxygen atoms. For $(x_O, y_O, z_O)$ close to $(-0.03, 0.05, 0.15)$, which are the most common choice in the literature, the chosen positions of Oxygens $a_1$ and $e_1$ are $a (1/8 - x_O, y_O + z_O - 1/4)/\sqrt{2}, (y_O - z_O + 1/4)/\sqrt{2}$ and $(z_O - 1/8, 1/8 - x_O - y_O)/\sqrt{2}, (1/4 + x_O - y_O)/\sqrt{2}$ and the position of Ce is $(1/2, 0, 0)$, which allow to compute $\vec{r}_{a_1}$ and $\vec{r}_{e_1}$. With these, $d_1, S_1, S_2, \ldots S_6$, or $d_{ref}$ and $S_1 = 0, S_2, \ldots S_6$ are calculated as described above. For other choices of $(x_O, y_O, z_O)$, we can first find the equivalent position close to $(-0.03, 0.05, 0.15)$ and then do as it was just described. For instance, the experimental data (0.0351, 0.0538, 0.6578) of Lu$_2$CaMg$_2$Si$_3$O$_{12}$ (Ref. 4) can be seen as the $(-x, y, z + 1/2)$ equivalent position of $(-0.0351, 0.0538, 0.1578)$.

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Table I: Definitions of the $D_2$ totally symmetric displacements of the CeO$_8$ moiety chosen in this work. Stretching, bending, and twisting $O_h$ symmetry coordinates. The labels of the oxygen atoms and the chosen cartesian axes are defined in Fig. 1: In the reference cube, the symmetry independent oxygen atoms $a_1$ and $e_1$ are located at $(\sqrt{2}, 0, 1)d/\sqrt{3}$ and $(0, \sqrt{2}, 1)d/\sqrt{3}$ respectively, with $d$ being the Ce-O distance. $\hat{R}$ is the $D_2$ symmetrization operator: the normalized addition of the group symmetry operations (the identity and the three 180° rotations around the cartesian axes). $\delta x_{a_1}$ is the x cartesian displacement of the Oxygen atom $a_1$ from its position in the reference cube: $\delta x_{a_1} = x_{a_1} - x_{a_1,\text{ref}}$; identical definitions stand for the other cartesian displacements.

<table>
<thead>
<tr>
<th>Displacement</th>
<th>$O_h$ irrep</th>
<th>$\hat{R} = \frac{1}{2} \left( I + \hat{C}<em>{2x} + \hat{C}</em>{2y} + \hat{C}_{2z} \right)$</th>
<th>Definition</th>
</tr>
</thead>
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<td>symmetric stretching</td>
<td>$a_{1g}$</td>
<td>$S_1 = \frac{1}{\sqrt{6}} \hat{R} \left[ (\sqrt{2} \delta x_{a_1} + \delta z_{e_1}) + (\sqrt{2} \delta y_{e_1} + \delta z_{e_1}) \right]$</td>
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<td>asymmetric stretching</td>
<td>$e_g$</td>
<td>$S_2 = \frac{1}{\sqrt{6}} \hat{R} \left[ (\sqrt{2} \delta x_{a_1} + \delta z_{e_1}) - (\sqrt{2} \delta y_{e_1} + \delta z_{e_1}) \right]$</td>
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<tr>
<td>symmetric bending</td>
<td>$e_g$</td>
<td>$S_3 = \frac{1}{\sqrt{6}} \hat{R} \left[ -\delta x_{a_1} + \sqrt{2} \delta z_{e_1} \right] + \left[ -\delta y_{e_1} + \sqrt{2} \delta z_{e_1} \right]$</td>
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<tr>
<td>asymmetric bending</td>
<td>$e_g$</td>
<td>$S_4 = \frac{1}{\sqrt{6}} \hat{R} \left[ -\delta x_{a_1} + \sqrt{2} \delta z_{e_1} \right] - \left[ -\delta y_{e_1} + \sqrt{2} \delta z_{e_1} \right]$</td>
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<tr>
<td>symmetric twisting</td>
<td>$e_u$</td>
<td>$S_5 = \frac{1}{\sqrt{2}} \hat{R} \left[ -\delta y_{a_1} + \delta x_{e_1} \right]$</td>
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<tr>
<td>asymmetric twisting</td>
<td>$e_u$</td>
<td>$S_6 = \frac{1}{\sqrt{2}} \hat{R} \left[ \delta y_{a_1} + \delta x_{e_1} \right]$</td>
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<td>Ref.</td>
<td>$a$ (Å)</td>
<td>$x_0$</td>
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<td>-----------</td>
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<td>6</td>
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<tr>
<td>YbAG</td>
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<td>6</td>
<td>12.0000</td>
<td>-0.03060</td>
</tr>
<tr>
<td>GdAG</td>
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<td>12.1130</td>
<td>-0.03110</td>
</tr>
<tr>
<td>LuGG</td>
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<td>12.1880</td>
<td>-0.02520</td>
</tr>
<tr>
<td>YbGG</td>
<td>6</td>
<td>12.2040</td>
<td>-0.02590</td>
</tr>
<tr>
<td>YGG</td>
<td>37</td>
<td>12.2730</td>
<td>-0.02740</td>
</tr>
<tr>
<td>HoGG</td>
<td>38</td>
<td>12.2900</td>
<td>-0.02740</td>
</tr>
<tr>
<td>DyGG</td>
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<td>-0.02780</td>
</tr>
<tr>
<td>TbGG</td>
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<td>12.3829</td>
<td>-0.02890</td>
</tr>
<tr>
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<td>12.4361</td>
<td>-0.02920</td>
</tr>
<tr>
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<td>12.5051</td>
<td>-0.03000</td>
</tr>
<tr>
<td>Pyrope</td>
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<td>11.4566</td>
<td>-0.03290</td>
</tr>
<tr>
<td>Almandine</td>
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<td>11.5230</td>
<td>-0.03401</td>
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<tr>
<td>Spessartine</td>
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<td>11.6190</td>
<td>-0.03491</td>
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<tr>
<td>Grossular</td>
<td>40</td>
<td>11.8515</td>
<td>-0.03760</td>
</tr>
<tr>
<td>Andradite</td>
<td>7</td>
<td>12.0578</td>
<td>-0.03940</td>
</tr>
<tr>
<td>Lu$_2$CaMg$_2$Si$_2$O$_12$</td>
<td>7</td>
<td>12.2500</td>
<td>-0.04004</td>
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</table>

TABLE III: $4f$ and $5d$ energy levels of Ce$^{3+}$-doped YAG (in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Level</th>
<th>This work $^a$</th>
<th>Ref. 8 $^b$</th>
<th>Difference $^c$</th>
<th>Level</th>
<th>This work $^a$</th>
<th>Ref. 8 $^b$</th>
<th>Difference $^c$</th>
<th>Experiment $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\Gamma_4$ $4f_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$8\Gamma_5$ $5d_1$</td>
<td>25680</td>
<td>24040</td>
<td>-1640</td>
<td>22000 $^e$</td>
</tr>
<tr>
<td>$2\Gamma_4$ $4f_2$</td>
<td>145</td>
<td>370</td>
<td>+225</td>
<td>$9\Gamma_5$ $5d_2$</td>
<td>29680</td>
<td>31660</td>
<td>+1980</td>
<td>29400 $^e$</td>
</tr>
<tr>
<td>$3\Gamma_4$ $4f_3$</td>
<td>900</td>
<td>820</td>
<td>-80</td>
<td>$10\Gamma_5$ $5d_3$</td>
<td>52350</td>
<td>48070</td>
<td>-4280</td>
<td>44000 $^e$</td>
</tr>
<tr>
<td>$4\Gamma_4$ $4f_4$</td>
<td>2280</td>
<td>2360</td>
<td>+80</td>
<td>$11\Gamma_5$ $5d_4$</td>
<td>53560</td>
<td>52540</td>
<td>-1020</td>
<td>48900 $^f$</td>
</tr>
<tr>
<td>$5\Gamma_4$ $4f_5$</td>
<td>2300</td>
<td>2570</td>
<td>+270</td>
<td>$12\Gamma_5$ $5d_5$</td>
<td>58900</td>
<td>54190</td>
<td>-4710</td>
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</tr>
<tr>
<td>$6\Gamma_4$ $4f_6$</td>
<td>2540</td>
<td>2810</td>
<td>+270</td>
<td>$7\Gamma_4$ $4f_7$</td>
<td>5650</td>
<td>4320</td>
<td>-1330</td>
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</tr>
</tbody>
</table>

$^a$Spin-orbit coupling calculation: Undistorted relaxation, first coordination shell effect only.

$^b$Ab initio calculations also including host specific embedding and structural relaxation.

$^c$Estimated effects of host specific embedding plus structural relaxation.

$^d$After the assignment analysis in Reference 35.

$^e$Reference 1.

$^f$Reference 43.
**Figure captions**

FIG. 1: $D_2$ totally symmetric displacements of the CeO$_8$ moiety: Stretching, bending, and twisting $O_h$ symmetry coordinates $S_1$ ($a_{1g}$ symmetric stretching -breathing-), $S_2$ ($e_g$ asymmetric stretching), $S_3$ ($e_g$ symmetric bending), $S_4$ ($e_g$ asymmetric bending), $S_5$ ($e_u$ symmetric twisting), and $S_6$ ($e_u$ asymmetric twisting). See Table I for the detailed definitions.

FIG. 2: 4$f$ (dashed lines) and 5$d$ (full lines) energy levels of the (CeO$_8$)$_{13}^-$ embedded cluster (relative to the ground state) as a function of the $S_1 - S_6$ $D_2$ oxygen displacement coordinates, calculated without spin-orbit coupling. The differences between the 5$d$ and 4$f$ energy centroids (dot-dashed lines) and between the ligand field stabilization energies of the 5$d$ and 4$f$ lowest levels (doted lines) are also shown; the lowest 4$f$ → 5$d$ transition equals the subtraction of these two. Experimental values of $S_1 - S_6$ of 21 pure garnets are shown as small vertical lines.

FIG. 3: 4$f$ and 5$d$ energy levels of the (CeO$_8$)$_{13}^-$ embedded cluster as a function of $S_1 - S_6$, calculated with spin-orbit coupling. All levels are $D'_2 \Gamma_5$ Kramer doublets. See Fig. 2 caption.

FIG. 4: 4$f$ energy levels of the (CeO$_8$)$_{13}^-$ embedded cluster as a function of $S_1 - S_6$, calculated without spin-orbit coupling. Dotted lines: $^3A$ levels; full lines: $^3B_1$ levels; dashed lines: $^2B_2$ and $^2B_3$ levels. Experimental values of $S_1 - S_6$ of 21 pure garnets are shown as small vertical lines.

FIG. 5: 4$f$ energy levels of the (CeO$_8$)$_{13}^-$ embedded cluster as a function of $S_1 - S_6$, calculated with spin-orbit coupling. All levels are $D'_2 \Gamma_5$ Kramer doublets. Experimental values of $S_1 - S_6$ of 21 pure garnets are shown as small vertical lines.
Figure 2. Seijo and Barandiarán
Figure 3. Seijo and Barandiarán
Figure 4. Seijo and Barandiarán
Figure 5. Seijo and Barandiarán