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Reference


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Effect of the f-Orbital Delocalization on the Ligand-Field Splitting Energies in Lanthanide-Containing Elpasolites

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Abstract: The ligand-field induced splitting energies of f-levels in lanthanide-containing elpasolites are derived using the first-principles universal orbital-free embedding formalism [Wesolowski and Warshel, J. Phys. Chem. 1993, 97, 8050]. In our previous work concerning chloroelpasolite lattice (Cs₂NaLnCl₆), embedded orbitals and their energies were obtained using an additional assumption concerning the localization of embedded orbitals on preselected atoms leading to rather good ligand-field parameters. In this work, the validity of the localization assumption is examined by lifting it. In variational calculations, each component of the total electron density (this of the cation and that of the ligands) spreads over the whole system. It is found that the corresponding electron densities remain localized around the cation and the ligands, respectively. The calculated splitting energies of f-orbitals in chloroelpasolites are not affected noticeably in the whole lanthanide series. The same computational procedure is used also for other elpasolite lattices (Cs₂NaLnX₆, where X=F, Br, and I)—materials which have not been fabricated or for which the ligand-field splitting parameters are not available.

1. Introduction

Lanthanide complexes offer potential applications in chemistry, physics, and other related areas.1–13 Theoretical modeling of such complexes involves high-cost methods because of the role of electron correlation and the necessity of taking into account the effects of the environment of the f-elements.14–29 Density-functional-theory methods based on the Kohn–Sham equations (KS-DFT) became standard tools in modeling large polyatomic systems.30–32 In practice, KS-DFT calculations apply approximations to the exchange-correlation functional and the associated potential which are usually rather adequate. Typically, they lead to results of reasonable accuracy at computational cost which is significantly lower than that of traditional wave function-based methods. For some systems and/or properties, however, standard approximations face difficulties. As far as the f-elements are concerned, they lead to rather satisfactory results concerning structure, energetics, and vibrational properties33–35 but lead sometimes to qualitatively wrong results as far as the details of the electronic structure are concerned.36–41 Alternatively, following the spirit of the ligand-field theory, the orbitals of key interest can be obtained using the embedding strategy, in which only the lanthanide is described at the orbital level, whereas its environment is represented by some “effective embedding potential”.42–46 In this work, we apply the nonempirical embedding formalism48 in which the embedded subsystem is described at the orbital level, whereas its environment is characterized by the electron density (ρᵢ). For a given ρᵢ, the embedded orbitals (φᵢ) used to construct the electron density of the subsystem under investigation (ρᵢ = Σᵢ=1ᴺᵢ|φᵢ⟩|^2) are obtained from one-electron Kohn–Sham-like equations:48

\[ \left[ \frac{-1}{2} \nabla^2 + V_{\text{eff}}^{\text{KSCED}} \right] \phi_{M,i} = \epsilon_{M,i} \phi_{M,i} \]  (1)

The superscript KSCED (Kohn–Sham Equations with Constrained Electron Density) is used to indicate the difference between the effective potential in eq 1 and that in the

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Kohn–Sham formalism.\textsuperscript{31} Fully variational variant of the
above scheme, where instead of assuming some $\rho_l$ it is obtained from a
complementary embedding equation in which $\rho_l$ and $\rho_{li}$ exchange their
roles, represents one of the possible practical realizations of the subsystem
formulation of density functional theory by Cortona.\textsuperscript{47} The total effective
potential $V^\text{KSCED}(\rho_l, \rho_{li})$ can be conveniently split into two
components: the Kohn–Sham effective potential for the
isolated subsystem ($V^\text{KS}(\rho_l, \rho_{li})$) and the remaining part
representing the environment ($V^\text{emb}(\rho_l, \rho_{li})$) which reads

$$V^\text{eff}_{\text{emb}}(\rho_l, \rho_{li}) = \sum_{\lambda l} \left( \frac{Z_{\lambda l}}{|\mathbf{r} - \mathbf{R}_{\lambda l}|} + \int \frac{\rho_l(r')}{|\mathbf{r}' - \mathbf{R}_{\lambda l}|} d\mathbf{r}' + \frac{\delta E_{\text{xc}}[\rho_l + \rho_{li}]}{\delta \rho_l} - \frac{\delta E_{\text{xc}}[\rho_l]}{\delta \rho_l} + \frac{\delta T^\text{rad}_{\lambda l}[\rho_l, \rho_{li}]}{\delta \rho_l} \right)$$

where $T^\text{rad}_{\lambda l}[\rho_l, \rho_{li}] = T_s[\rho_l + \rho_{li}] - T_s[\rho_l]$, and $T_s[\rho_l]$ and the
functionals $E_{\text{xc}}[\rho]$ and $T_s[\rho]$ are defined in the Kohn–Sham
formalism.\textsuperscript{31} Neither $V^\text{KS}(\rho_l, \rho_{li})$ nor $V^\text{eff}_{\text{emb}}(\rho_l, \rho_{li})$ depend on
the orbitals but only on the electron densities of the two
subsystems.

The numerical solution of eq 1 proceeds by representing
embedded orbitals as a linear combination of atom-centered
basis functions ($\{\chi^j\}$ and $\{\chi^{j,l}\}$). In such a case, two types of
expansion are of great practical relevance: the approximated
one, in which only selected atom-centered functions are used
in the construction of embedded orbitals, and another one,
in which all available atom-centered functions are used. The
first type of expansion is an approximation, and such
calculations are labeled here by KSCED(m) following
the convention of ref 49. It was used in our previously reported
work on the ligand-field parameters of the $f$-levels of
lanthanide cations in chloroelpasolites. It is referred to also
as “monomolecular expansion”. This type of expansion is
obviously attractive computationally. Its drawback is, how-
ever, the absence of the terms of the $\chi^j(r)\chi^{j,l}(r)$ type in
the expansion of the total electron density ($\rho_{\text{total}} = \rho_l + \rho_{li}$). This
makes the cases with possible intersubsystem charge-transfer
and/or covalency computationally unattractive because of
the very slow convergence of the KSCED(m) results with the
basis set.\textsuperscript{50}

Our previous studies showed that the differences between
ligand-field splitting energies derived from KSCED(m)
calculations and deduced from experiment\textsuperscript{52} were rather small
(relative errors withing 10–20%).\textsuperscript{53} Such errors are qualifi-
catively smaller than the ones corresponding to calculations
applying conventional Kohn–Sham calculations or electro-
static-only embedding.\textsuperscript{51} Several factors contribute to the
deviations from experimental data: the intrinsic errors in the
applied approximation for the exchange-correlation effective
potential, the use of the average-of-configuration reference
state, errors in the applied approximation to the nonadditive
kinetic energy effective potential, and the absence of the
$\chi^j(r)\chi^{j,l}(r)$ terms.

In the present work, one among possible sources of
deviations between the calculated and experimental param-
eters reported previously is investigated in detail. The effect
of charge transfer and covalency is quantified by comparing
the ligand-field splitting energies derived from the two types of
KSCED embedding calculations which use either monom-
er or supermolecular expansion of both components of the
total electron density ($\rho_l$ and $\rho_{li}$). Following the convention
of ref 49, the calculations using the supermolecular expansion
are labeled by KSCED(s) in this work.

It is worthwhile to notice that the possibility for a complete
delocalization of $f$-orbitals and charge transfer might either
improve or worsen the calculated splitting energy. The
worsening of the results would indicate that the applied
approximation functionals in the embedding potential given
in eq 2 are not adequate, and their flaws are exposed by
adding more flexibility to the embedded orbitals. One of the
key issues of this work is, therefore, the determination
whether the good quality of the obtained previously KSCED-
(m) results is due to the localization assumption. This
assumption is no longer made in the present work. The
possibility of the intersystem charge-flow exposes the
possible flaws of the approximations used in the embedding
potential given in eq 2 such as an artificial charge-leak from
ligands to the cation.\textsuperscript{51} Due to the variational character of
the applied method, the use of more centers in the orbital
expansion leads to the results which are closer to the basis
set limit. It is especially important in view of the possible
extension of the present studies toward modeling the
complete spectra of lanthanide centers in solids. Such a task
hinges, however, not only on a reliable description of the
effect of the environment—the main issue of this work—but
also on a proper representation of the electronic structure of
the isolated cation.

2. Computational Details

Applications of eqs 1 and 2 in computer modeling rely on
the approximations to the relevant functionals: $T^\text{rad}_{\lambda l}[\rho_l, \rho_{li}]$ and
$E_{\text{xc}}[\rho_l]$. The used functionals approximate reasonably well
the exact embedding potential of eq 2 in the case of small
overlap between the electron densities $\rho_l$ and $\rho_{li}$. The applied
gradient-dependent approximation for $T^\text{rad}_{\lambda l}[\rho_l, \rho_{li}]$ was chosen
based on dedicated numerical tests in the case of such
couples of $\rho_l$ and $\rho_{li}$,\textsuperscript{49} which do no overlap significantly—a
case relevant for the present studies.

The exchange-correlation component of the effective
embedding potential given in eq 2 was approximated by
means of the functional of Perdew and Wang (PW91).\textsuperscript{54} The
van Leeuwen-Baerends (LB94) exchange-correlation potential\textsuperscript{55} was used to approximate the exchange-correlation
component of $V^\text{KS}(\rho_l, \rho_{li})$ in eq 1. This choice was motivated
by the fact that one component of the system (ligands) is
negatively charged, and such systems are not well described
by means of the Kohn–Sham equations applying semilocal
functionals. The orbital-free embedding potential given in
eq 2 depends not only on the choice of the approximations
used to evaluate its exchange-correlation- and kinetic-energy
dependent components but also on the choice of the electron
density $\rho_{li}$. All the reported numerical values were obtained
from fully variational calculations in which both $\rho_{li}$ and $\rho_{li}$
are derived from the minimization of the total-energy
bifunctional $E[\rho_l, \rho_{li}]$ in eq 2. Such a minimization is
the orbitals of the ligands were obtained from eq 1 in which $F_I$ corresponds to the environment. The numerical implementation of eqs 1 and 2 into the Amsterdam Density Functional (ADF) package was used in all calculations. Relativistic scalar ZORA, all electron calculations were performed using the ZORA triple-$\zeta$ STO set plus one polarization function (ZORA/TZP). Figure 1 shows the investigated system comprising the octahedral arrangement of the lanthanide cation $\text{Ln}^{3+}$ and its ligands. $O_h$ symmetry was assumed in all calculations.

Figure 2. The f-orbital levels of $\text{Ln}^{3+}$ in the octahedral environment.

performed by means of the “freeze-and-thaw” cycle of iterations described in ref 56.

The orbital-levels of an embedded lanthanide cation ($\text{Ln}^{3+}$) were obtained from eq 1 in which $p_I$ corresponds to $\text{Ln}^{3+}$ and $p_{II}$ to the environment. The numerical implementation of eqs 1 and 2 into the Amsterdam Density Functional (ADF) package was used in all calculations. Relativistic scalar ZORA, all electron calculations were performed using the ZORA triple-$\zeta$ STO set plus one polarization function (ZORA/TZP). Figure 1 shows the investigated system comprising the octahedral arrangement of the lanthanide cation $\text{Ln}^{3+}$ and its ligands. $O_h$ symmetry was assumed in all calculations.

Figure 2 shows the expected order of f-levels ($d_{2g}$, $t_{2g}$, and $t_{1u}$) and defines the two ligand-field splitting parameters $\Delta_1$ and $\Delta_2$. The energy levels were calculated for average-of-configuration, in which each f-orbital was partially occupied (occupation number ($n_f/7$)) for a given $f^n$ configuration. The occupations of orbitals used to express the electron density of the ligands ($p_{II}$) were chosen in such a way that the corresponding single-determinantal wave function possesses the full symmetry of the system. In some cases ($\text{Ln}=\text{Ce, Pr, Nd, and Sm in Cs}_2\text{NaLnX}_6$), the orbitals of the ligands were maximally filled (occupations given in Table 1). The $N_{\text{electrons}}$ orbitals ($N_{\text{orb}} = 2, 4, 7$ and $8$ corresponding to X=F, Cl, Br, and I in $\text{Cs}_2\text{NaLnX}_6$, respectively) were, therefore, emptied.

3. Results and Discussion

This section comprises two parts. In the first one, the results of KSCED(s) and KSCED(m) calculations are compared in order to show the role of f-orbital delocalization on the calculated ligand-field splitting energies. The following section concerns the ligand-field splitting energies for a number of other elpasolites, for which either experimental ligand-field splitting were not accurately measured yet, or for materials which do not exist.

Table 2 collects the ligand-field splitting parameters $\Delta_1$ and $\Delta_2$ in lanthanide-containing chloroelpasolites $\text{Cs}_2\text{NaLnCl}_6$ derived from KSCED(m) and KSCED(s) calculations (see also Figure 3). Experimental results are also given for the sake of comparison. Note that the $\Delta_1$ and $\Delta_2$ values given in refs 40 and 53 for Yb (220 and 799 cm$^{-1}$, respectively) are erroneous, and we use the correct ones (301 and 747 cm$^{-1}$, respectively) here. In the whole lanthanide series, lifting the localization assumption for embedded orbitals does not affect significantly the calculated values of $\Delta_1$. Both KSCED(m) and KSCED(s) results are very similar and agree very well with experiment. The experimental values of $\Delta_1$ decrease almost monotonically in the whole series from 390 cm$^{-1}$ (Ce) to 301 cm$^{-1}$ (Yb). However, the dependence of the calculated values of $\Delta_1$ on the number of f-electrons $n_f$ is smoother than that deduced from experiment. The average and the maximal deviation from experimental data amount to 28 and 100 cm$^{-1}$ (Sm) using the KSCED(m) scheme and 50 and 201 cm$^{-1}$ (Ce) using KSCED(s), respectively. The corresponding mean absolute errors amount to 52 and 83 cm$^{-1}$.

Compared to $\Delta_1$, the effect of lifting the localization assumption on $\Delta_2$ is different. For cations with $n_f > 7$, the KSCED(m) and KSCED(s) values are almost identical. For $n_f < 7$ cations, the possibility of delocalization increases the calculated $\Delta_2$ parameter by about 100 cm$^{-1}$ bringing the calculated values closer to the experimental data.

The average and the maximal deviation from the experimental data amount to 178 and 320 cm$^{-1}$ (Eu) for KSCED(m) and 141 and 315 cm$^{-1}$ (Ho) for KSCED(s), respectively. The corresponding mean absolute errors amount to 100 and 168 cm$^{-1}$.

Table 1: Electronic Occupation Numbers of the Hexahalide Anions for Each Irreducible Representation of the $O_h$ Symmetry

<table>
<thead>
<tr>
<th>irrep/halides</th>
<th>(F$^-$)$_6$</th>
<th>(Cl$^-$)$_6$</th>
<th>(Br$^-$)$_6$</th>
<th>(I$^-$)$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>6</td>
<td>10</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$E_g$</td>
<td>12</td>
<td>20</td>
<td>36</td>
<td>52</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>6</td>
<td>12</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>6</td>
<td>12</td>
<td>30</td>
<td>48</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$E_u$</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>24</td>
<td>42</td>
<td>72</td>
<td>102</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>6</td>
<td>12</td>
<td>30</td>
<td>48</td>
</tr>
<tr>
<td>$N_{\text{electrons}}$</td>
<td>60</td>
<td>108</td>
<td>216</td>
<td>324</td>
</tr>
</tbody>
</table>
The small differences between the KSCED(m) and KSCED(s) results (¢1 and ¢2) for the whole series of embedded lanthanide cations, indicate clearly that lifting the localization assumption does not affect significantly the orbital levels. In some cases, the agreement between the calculated and experimental ligand-field splitting parameters slightly improves. As measured by mean absolute errors in the whole lanthanide series, lifting the localization assumption leads only to a slight deterioration of the calculated splitting energies. It is worthwhile to stress at this point that the intersystem charge-flow possible in KSCED(s) calculations makes the KSCED embedding potential prone to possible flaws of the applied approximations in the relevant functionals.51 Moreover, the KSCED(s) results approach better the basis set limit for the applied method which is based on the variational principle. The remaining deviations between the KSCED calculated and experimental parameters should be attributed to other assumptions/approximations used in the applied computational scheme: the use of average-of-configurations and approximations for the exchange-correlation- and nonadditive-kinetic-energy potentials.

In the following part, the results were obtained for a number of other elpasolites for which either experimental splitting parameters were not accurately measured yet or do not exist.

|-----------------------------------|---------------------------------------------|

Table 2: Experimental and Calculated Ligand-Field Splitting Parameters Δ1 and Δ2 (in cm⁻¹) Derived from KSCED(s) and KSCED(m) Calculations

<table>
<thead>
<tr>
<th>Element</th>
<th>KSCED(s) Δ1 (cm⁻¹)</th>
<th>KSCED(s) Δ2 (cm⁻¹)</th>
<th>KSCED(m) Δ1 (cm⁻¹)</th>
<th>KSCED(m) Δ2 (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>390</td>
<td>462</td>
<td>370</td>
<td>430</td>
</tr>
<tr>
<td>Pr</td>
<td>343</td>
<td>400</td>
<td>320</td>
<td>380</td>
</tr>
<tr>
<td>Nd</td>
<td>250</td>
<td>310</td>
<td>230</td>
<td>290</td>
</tr>
<tr>
<td>Pm</td>
<td>341</td>
<td>350</td>
<td>320</td>
<td>330</td>
</tr>
<tr>
<td>Sm</td>
<td>300</td>
<td>350</td>
<td>270</td>
<td>320</td>
</tr>
<tr>
<td>Eu</td>
<td>299</td>
<td>300</td>
<td>270</td>
<td>280</td>
</tr>
<tr>
<td>Gd</td>
<td>301</td>
<td>300</td>
<td>270</td>
<td>280</td>
</tr>
<tr>
<td>Tb</td>
<td>358</td>
<td>350</td>
<td>320</td>
<td>330</td>
</tr>
<tr>
<td>Dy</td>
<td>300</td>
<td>300</td>
<td>270</td>
<td>280</td>
</tr>
<tr>
<td>Ho</td>
<td>299</td>
<td>300</td>
<td>270</td>
<td>280</td>
</tr>
<tr>
<td>Er</td>
<td>299</td>
<td>300</td>
<td>270</td>
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<td>Tm</td>
<td>301</td>
<td>300</td>
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<td>280</td>
</tr>
<tr>
<td>Yb</td>
<td>301</td>
<td>300</td>
<td>270</td>
<td>280</td>
</tr>
</tbody>
</table>

Calculations were made at the ab initio optimized ion–ligand distances.
in the expected order along the series I<Br<Cl<F. It is worthwhile to note that the ligand–cation (X–Ln\(^{3+}\)) distance increases along the series F, Cl, Br, and I. Except for iodide elpasolites Cs\(_2\)NaLnI\(_6\), the numerical values derived from KSCED(s) and KSCED(m) calculations are very similar. This exceptional behavior of iodide elpasolites Cs\(_2\)NaLnI\(_6\) results probably from the fact that iodine has the smallest electron affinity among the considered ligands. In view of the analysis concerning chloroelpasolites, the numerical values derived from KSCED(s) calculations are probably more accurate.

4. Conclusions

In this study, the ligand-field splitting parameters \(\Delta_1\) and \(\Delta_2\) obtained from orbital-free embedding calculations are reported. To take into account the f-orbital delocalization and the possibility of the ligand \(**\) metal charge transfer, supermolecular expansion of basis sets functions was used for each subsystem. The results obtained previously using selected atom-centered functions in the linear combination of atomic orbitals expansion of embedded orbitals (monomolecular expansions for \(\rho_l\) and \(\rho_{Ln}\)) are not affected for heavier lanthanides (\(f_n > 7\)) and are slightly improved for lighter ones (\(f_n < 7\)) in chloroelpasolites. Our calculations confirm that localizing the cation and ligand orbitals in different regions in space, an intuitive approximation applied in our previous work, is adequate because lifting this assumption does not affect the calculated parameters significantly. Nevertheless, the calculated difference between the \(t_{2g}\) and \(a_{2g}\) levels (\(\Delta_2\) parameter) is underestimated by about 200 cm\(^{-1}\) for cations with the f-shell more than half-filled. This underestimation is probably the result of the use of the “average-of-configuration” Ansatz or the inherent errors of the applied approximations for the effective potential in KSCED. The present analysis does not justify a more precise determination of the relative significance of these two effects. Another possible source of deviations between the ligand-field parameters deduced from experiment and the calculated ones might be the result of their strong dependence (\(r^{-3} - r^{-6}\)) on the metal–ligand distances. In fact, the actual geometry in the crystal lattice might be different from the standard geometries applied in this work. The current study provides also predictions of the ligand-field splitting parameters for homologous materials: fluoroelpasolites Cs\(_2\)NaLnF\(_6\), bromoelpasolites Cs\(_2\)NaLnBr\(_6\), and iodoelpasolites Cs\(_2\)NaLnI\(_6\). The KSCED(s) results are recommended because the additional atom-centered basis functions approach better the complete basis set, whereas their use was found to be numerically stable despite possible flaws in the used approximations for the orbital-free embedding potential given in eq 2.

**Acknowledgment.** This work is supported by the Swiss National Science Foundation. It is also part of the COST D26 Action.

**References**


**Table 3:** Ligand-Field Splitting Parameters \(\Delta_1\) and \(\Delta_2\) (in cm\(^{-1}\)) from KSCED(m) Calculations Using the Sum of Ionic Radii Cation–Ligand Distances\(^{64}\)

<table>
<thead>
<tr>
<th>Cation</th>
<th>(\Delta_1)</th>
<th>(\Delta_2)</th>
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<tbody>
<tr>
<td>(F^-)</td>
<td>782</td>
<td>380</td>
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<tr>
<td>(Cl^-)</td>
<td>720</td>
<td>349</td>
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<tr>
<td>(Br^-)</td>
<td>651</td>
<td>313</td>
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<td>(I^-)</td>
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<td>291</td>
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<td>(F^-)</td>
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<td>(Cl^-)</td>
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<td>(Br^-)</td>
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<td>248</td>
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<tr>
<td>(I^-)</td>
<td>532</td>
<td>249</td>
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**Table 4:** Ligand-Field Splitting Parameters \(\Delta_1\) and \(\Delta_2\) (in cm\(^{-1}\)) from KSCED(s) Calculations Using the Sum of Ionic Radii Cation–Ligand Distances\(^{64}\)

<table>
<thead>
<tr>
<th>Cation</th>
<th>(\Delta_1)</th>
<th>(\Delta_2)</th>
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<tbody>
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<td>(F^-)</td>
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<td>(Br^-)</td>
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<td>(I^-)</td>
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