Influence of charge transfer in 3d perovskite oxides

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3d perovskite oxides
   Influence of Temperature and pressure on CaFeO$_3$ crystal

Embedded cluster approach

Pressure induced high spin to low spin transition
   Unitary transformation of the active orbitals
   Charge transfer with increasing pressure

Charge Disproportionation

Analysis of Mössbauer spectroscopy

Conclusions
**3d perovskite oxides**

**Jahn-Teller distortion**
- LaMnO$_3$  Mn$^{3+}$ 3d$^4$  Pbnm  $T_{JT} = 750$ K
- d$^4$ systems $\rightarrow$ Jahn-Teller distortion is expected

**Bonding canonical orbitals**
- Antibonding canonical $\ast$ orbitals

**Charge disproportionation**
- CaFeO$_3$  Fe$^{4+}$ 3d$^4$  Pbnm to P$_{2_{1}/n}$  $T_{CD} = 298$ K

Table I: metal-ligand bond lengths in angstrom.

<table>
<thead>
<tr>
<th></th>
<th>LaMnO$_3$</th>
<th>CaFeO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>798 K</td>
</tr>
<tr>
<td>TM-O(1)</td>
<td>1.968</td>
<td>2.010</td>
</tr>
<tr>
<td>TM-O(2)</td>
<td>1.907</td>
<td>1.998</td>
</tr>
<tr>
<td>TM-O(3)</td>
<td>2.178</td>
<td>2.035</td>
</tr>
</tbody>
</table>
Influence of temperature on $\text{CaFeO}_3$ crystal

Mössbauer spectroscopy

0.048 mm/s
$\text{Fe}^{4+}\text{O}^{-}\text{Fe}^{4+}$

-0.026 0.310 mm/s
$\text{Fe}^{5+}\text{O}^{-}\text{Fe}^{3+}$

Influence of pressure on $\text{CaFeO}_3$ crystal

X-ray diffraction

$\text{CaFeO}_3$ lattice parameters and average Fe-O distance in Angstrom with increasing pressure. The parameters are deduced from Woodward et al, PRB (2000) for 0.1 GPa and Fig. 2 in Takano et al, PRL (1991) for larger pressure.

<table>
<thead>
<tr>
<th></th>
<th>0.1 GPa</th>
<th>10 GPa</th>
<th>20 GPa</th>
<th>30 GPa</th>
<th>40 GPa</th>
<th>50 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.31744</td>
<td>5.24673</td>
<td>5.17602</td>
<td>5.09117</td>
<td>5.16195</td>
<td>5.16100</td>
</tr>
<tr>
<td>b</td>
<td>5.31744</td>
<td>5.24673</td>
<td>5.17602</td>
<td>5.09117</td>
<td>4.89325</td>
<td>4.83668</td>
</tr>
<tr>
<td>c</td>
<td>7.52000</td>
<td>7.42000</td>
<td>7.32000</td>
<td>7.20000</td>
<td>7.20010</td>
<td>7.09000</td>
</tr>
<tr>
<td>Fe-O</td>
<td>1.918</td>
<td>1.889</td>
<td>1.865</td>
<td>1.833</td>
<td>1.819</td>
<td>1.803</td>
</tr>
</tbody>
</table>

Mössbauer spectroscopy

The ambient pressure spectrum consists of a single narrow line with a chemical shift of 0.048 mm/s.

Chemical shift is reduced abruptly at 30 GPa by 0.25 mm/s

Pressure induced high spin to low spin transition
Basic Cluster: MLn
Basis set: O 4s3p1d ANO
Fe 6s5p4d1f ANO

Model Potentials: \textit{ab initio} Embedded Model Potentials AIEMP (based on Theory of Electron Separability).

Point charges: long range electrostatic interactions with a set of optimized point charges to reproduce the Madelung field in the cluster region arising from the rest of the crystal.
Embedded cluster approach: Cluster wave function

SCF: single determinant description of the electronic function

Molecular orbitals \( \varphi_i = \sum_k \lambda_{ki} \chi_k \)

Determinant \( \phi_j = |\varphi_1\varphi_2...\varphi_N \rangle \)

HF solution \( E = \min \lambda_{ki} \frac{\langle \phi \mid \hat{H} \mid \phi \rangle}{\langle \phi \mid \phi \rangle} \)

CASSCF: Adequate description of the electron distribution

\[ |\Psi_m \rangle = \sum_l c_{lm} |\Phi_l \rangle \]

\( E = \min_{c_{lm}, \lambda_{ki}} \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} \)

CASPT2: Accurate description of the relative energies of the different electronic states (Perturbation method applied on the CASSCF wave function)
<table>
<thead>
<tr>
<th>State</th>
<th>Dominant electronic configuration</th>
<th>CAS(8,12)SCF + CASPT2</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5E_g$</td>
<td>$e_g^4 t_{2g}^* e_g^1$</td>
<td></td>
<td>0.00 ; 0.04</td>
</tr>
<tr>
<td>$a^3T_{1g}$</td>
<td>$e_g^4 t_{2g}^4 e_g^0$</td>
<td></td>
<td>0.46 ; 0.50 ; 0.52</td>
</tr>
<tr>
<td>$^1T_{2g}$</td>
<td>$e_g^4 t_{2g}^4 e_g^0$</td>
<td></td>
<td>1.98 ; 1.99 ; 2.02</td>
</tr>
<tr>
<td>$^1E_y$</td>
<td>&quot;</td>
<td></td>
<td>2.16 ; 2.19</td>
</tr>
<tr>
<td>$^3E_g$</td>
<td>$e_g^4 t_{2g}^3 e_g^1$</td>
<td></td>
<td>2.26 ; 2.30</td>
</tr>
<tr>
<td>$b^3T_{1g}$</td>
<td>&quot;</td>
<td></td>
<td>2.72 ; 2.72 ; 2.74</td>
</tr>
<tr>
<td>$^3T_{2g}$</td>
<td>&quot;</td>
<td></td>
<td>2.82 ; 2.82 ; 2.82</td>
</tr>
<tr>
<td>$^5T_{2g}$</td>
<td>$e_g^4 t_{2g}^2 e_g^2$</td>
<td></td>
<td>3.42 ; 3.43 ; 3.47</td>
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Pressure induced High spin to low spin transition

*Takano et al, PRL (1991)*

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**CAS(8,12)SCF + CASPT2**

CASPT2 energies follow closely the Tanabe-Sugano diagram for a d⁴ ion in octahedral field.

At 25 GPa the ³T₁g state becomes the ground state of the system.

Agreement with experimental interpretation of the high spin to low spin transition for increasing pressure.

*A. Sadoc, C. de Graaf and R. Broer, PRB, 75, 165116 (2007)*
Unitary transformation

CaFeO$_3$  Fe$^{4+}$ d$^4$  Pbnm to P$_{2}/$n  $T_{CD} = 298$ K

Natural orbitals

\[ \begin{align*}
\uparrow & \quad e_g^* \quad 85.8 \% \quad e_g^4 \quad t_{2g}^* \quad e_g^1 \\
\uparrow & \quad t_{2g}^* \quad 7.2 \% \quad e_g^3 \quad t_{2g}^* \quad e_g^2 \\
\downarrow & \quad e_g \quad 4.4 \% \quad e_g^2 \quad t_{2g}^* \quad e_g^3 \\
\end{align*} \]

Formal charge = +4  \( \rightarrow \) \( {^5E_g} \) Ground state
CaFeO$_3$ Fe$^{4+}$ d$^4$ Pbnm to P$_{2}/$n T$_{CD}$ = 298 K CAS(8,12) or cas-pdd $^5$E$_g$ first root

$e_g^*$ mainly Fe-3d

$e_g$ mainly O-2p

Natural orbitals

$e_g^*$ 85.8% $e_g^4$ $t_{2g}^*^3$ $e_g^*$

$t_{2g}^*$ 7.2% $e_g^3$ $t_{2g}^*^3$ $e_g^*^2$

$e_g$ 4.4% $e_g^2$ $t_{2g}^*^3$ $e_g^*^3$

Formal charge = +4 $^5$E$_g$ Ground state

Effective number of Fe-3d electrons = 4.9

Effective charge = +3

GS corresponds to more than 60% of CT meaning that Fe ions are Fe$^{3+}$ with mainly $d^5$ L$^{-1}$ configuration

A. Sadoc, C. de Graaf and R. Broer, JCP, 126, 134709 (2007)
Clear decrease of CT configurations in the $^5E_g$ when the pressure is increased.

In the whole pressure range, the number of Fe-3d electrons is around 5.

For the triplet state, the NCT is less important and the DCT becomes twice as important compared to the $E_g$ state.
Charge Disproportionation

\[ \begin{align*}
0.048 \text{ mm/s} & \quad \text{Fe}^{4+} - \text{O} - \text{Fe}^{4+} \\
-0.026 \text{ mm/s} & \quad \text{Fe}^{5+} - \text{O} - \text{Fe}^{3+} \\
0.310 \text{ mm/s} & \\
\end{align*} \]

Nasu et al, Hyperfine Interactions (1992)

\[ d^4 \rightarrow d^3 + d^5 L^{-2} \]
Charge Disproportionation

Effective number of Fe-3d electrons = 4.9
Actual charge = +3
GS corresponds to more than 60% of CT meaning that Fe ions are Fe\(^{3+}\) with mainly d\(^5\) L\(^{-1}\) configuration

Table IV: Wave function expansion simulating CaFeO\(_3\) crystal using embedded cluster approach

<table>
<thead>
<tr>
<th>At 298 K, above (T_{CD})</th>
<th>NCT (d^4)</th>
<th>CT (d^5L^{-1})</th>
<th>DCT (d^6L^{-2})</th>
<th>Fe 3d-count</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18.9</td>
<td>66.2</td>
<td>13.9</td>
<td>4.93</td>
</tr>
</tbody>
</table>

Nasu et al, Hyperfine Interactions (1992)
Charge transfer with increasing temperature

Effective number of Fe-3d electrons = 4.9
Actual charge = +3

GS corresponds to more than 60 % of CT meaning that Fe ions are Fe\(^{3+}\) with mainly \(d^5 L^{-1}\) configuration

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<th>Fe 3d-count</th>
</tr>
</thead>
<tbody>
<tr>
<td>At 298 K, above (T_{CD})</td>
<td>18.9</td>
<td>66.2</td>
<td>13.9</td>
<td>4.93</td>
</tr>
<tr>
<td>At 15 K small octahedron</td>
<td>13.2</td>
<td>60.9</td>
<td>23.7</td>
<td>5.11</td>
</tr>
<tr>
<td>At 15 K large octahedron</td>
<td>9.4</td>
<td>65.3</td>
<td>23.3</td>
<td>5.14</td>
</tr>
</tbody>
</table>

We express the wave function with localized orbitals and calculate the number of electrons in the 3d shell which remains almost identical at 15K than as 300 K. This suggests that the transition metal ions keep the same effective charge in all temperature range.
### Analysis of Mössbauer spectroscopy

<table>
<thead>
<tr>
<th>cluster</th>
<th>$\rho$ (Fe)</th>
<th>IS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(H$_2$O)$_6^{2+}$</td>
<td>11819.158</td>
<td>1.39</td>
</tr>
<tr>
<td>FeF$_6^{4-}$</td>
<td>11819.011</td>
<td>1.34</td>
</tr>
<tr>
<td>FeCl$_4^{2-}$</td>
<td>11820.983</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe(H$_2$O)$_6^{3+}$</td>
<td>11822.936</td>
<td>0.5</td>
</tr>
<tr>
<td>FeF$_6^{3-}$</td>
<td>11822.432</td>
<td>0.48</td>
</tr>
<tr>
<td>FeCl$_4^{-}$</td>
<td>11823.592</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe(CN)$_6^{4-}$</td>
<td>11823.853</td>
<td>-0.02</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td>11824.160</td>
<td>-0.13</td>
</tr>
<tr>
<td>FeO$_4^{2-}$</td>
<td>11826.785</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

W. C. Nieuwpoort, D. Post, P. Th. van Duijnen PRB 17, 91 (1978)


Analysis of Mössbauer spectroscopy

\[ y = -0.2785x + 3293 \]
\[ R^2 = 0.99 \]
<table>
<thead>
<tr>
<th>cluster</th>
<th>Formal</th>
<th>Fe 3d-count</th>
<th>Eff charge</th>
<th>IS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(H₂O)₆²⁺</td>
<td>2+</td>
<td>6.05</td>
<td>1.95</td>
<td>1.39</td>
</tr>
<tr>
<td>FeF₆⁴⁻</td>
<td>2+</td>
<td>6.05</td>
<td>1.95</td>
<td>1.34</td>
</tr>
<tr>
<td>FeCl₄²⁻</td>
<td>2+</td>
<td>6.18</td>
<td>1.82</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe(H₂O)₆³⁺</td>
<td>3+</td>
<td>5.22</td>
<td>3.78</td>
<td>0.5</td>
</tr>
<tr>
<td>FeF₆³⁻</td>
<td>3+</td>
<td>5.19</td>
<td>3.81</td>
<td>0.48</td>
</tr>
<tr>
<td>FeCl₄⁻</td>
<td>3+</td>
<td>5.56</td>
<td>3.44</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe(CN)₆⁴⁻</td>
<td>2+</td>
<td>7.32</td>
<td>1.68</td>
<td>-0.02</td>
</tr>
<tr>
<td>Fe(CN)₆³⁻</td>
<td>3+</td>
<td>5.63</td>
<td>3.37</td>
<td>-0.13</td>
</tr>
<tr>
<td>FeO₄²⁻</td>
<td>6+</td>
<td>5.30</td>
<td>3.70</td>
<td>-0.69</td>
</tr>
</tbody>
</table>
Charge disproportionation

\[ y = -0.2785x + 3293 \]

\[ R^2 = 0.99 \]

Total density at the Fe nucleus

\( IS (\text{mm/s}) \)

-1.00
-0.50
0.00
0.50
1.00
1.50
2.00

11818
11819
11820
11821
11822
11823
11824
11825
11826
11827
11828

Large
Small

\( y = -0.2785x + 3293 \)

\( R^2 = 0.99 \)
Conclusions

Crossing high spin to low spin transition calculated at the CASPT2 level for 25 GPa. In agreement with Mössbauer experiment.

GS corresponds to more than 60 % of CT up to 30 GPa meaning that Fe ions are Fe$^{3+}$ with mainly d$^5$L$^{-1}$ configuration in CaFeO$_3$ crystal at room temperature.

Clear decrease of CT configurations in the $^5$E$_g$ when the pressure is increased.

No change of oxidation state for the Fe ions with increasing temperature in CaFeO$_3$ crystal as suggested by the term charge disproportionation.
Acknowledgments

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http://theochem.chem.rug.nl/

Coen de Graaf and Rosa Caballol
Department of Physical and Inorganic Chemistry
Universitat Rovira i Virgili, Tarragona

Thank you for your attention