Unusual layered order and charge disproportionation in double perovskite \( \text{Ca}_2\text{FeMnO}_6 \)

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While double perovskites \( \text{A}_2\text{B'B'O}_6 \), if ordered, usually form a rock-salt-type structure with a checkerboard \( \text{B'/B''} \) ordering, it is surprising that \( \text{Ca}_2\text{FeMnO}_6 \) has alternate \( \text{FeO}_2 \) and \( \text{MnO}_2 \) layers in its perovskite structure. Here we demonstrate, using density functional calculations, that this unusual layered ordering facilitates, and is largely helped by, the \( \text{Fe}^{3+}\text{-Fe}^{5+} \) charge disproportionation (CD) of the formal \( \text{Fe}^{4+} \) ions, which would otherwise be frustrated in the common rock salt structure. To further verify the important role of the CD for stabilization of this layered ordering, we carry out a comparative study for the isostructural \( \text{Ca}_2\text{TiMnO}_6 \) which has a simple \( \text{Ti}^{4+}\text{-Mn}^{4+} \) state free of the CD. Our calculations indicate that \( \text{Ca}_2\text{TiMnO}_6 \) instead prefers the standard rock salt structure to the layered one. Thus our study shows a nontrivial interplay between the CD and the type of ion ordering, and proves that the CD is strongly involved in stabilizing the unusual layered order of \( \text{Ca}_2\text{FeMnO}_6 \).

INTRODUCTION

When dealing with transition metal compounds one often looks at different degrees of freedom like charge, spin and orbital and their interplay with the lattice. An interesting phenomenon—charge disproportionation (CD)—occurs in the materials with a nominal integer valence which is however intrinsically unstable. In such systems there occurs a spontaneous charge segregation at low temperatures, for example, \( \text{CaFeO}_3 \) shows a CD (2\( \text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+} \)) at 290 K. A similar CD transition at 210 K is observed in the A-site (\( \text{Ca}, \text{Cu} \)) ordered perovskite \( \text{CaCu}_3\text{Fe}_4\text{O}_{12} \) with the nominal \( \text{Fe}^{4+} \). Below the CD transition temperature, the charge-disproportionated \( \text{Fe}^{3+} \) and \( \text{Fe}^{5+} \) ions at the B sites in a perovskite structure are usually ordered in a rock-salt manner. (Note that for the high valent transition metal ions and particularly those with a negative charge transfer energy, actually a large fraction of charges are here on ligand oxygens, i.e. for example \( \text{Fe}^{5+} \) is rather \( \text{Fe}^{3+} \text{L}^2 \), where \( \text{L} \) is a ligand hole, see e.g. Refs.). This however is not crucial for the further discussion, thus we will continue to speak about \( \text{Fe}^{5+} \) of course keeping in mind this remark).

The CD is observed structurally via the cooperative lattice distortion which accommodates the CD ions in different charge state and thus with different ionic size and bond length. It can also be identified by the Mössbauer spectrum. Moreover, this transition is often simultaneously accompanied by a metal-insulator transition: the formation of \( \text{Fe}^{3+}\text{-Fe}^{5+} \) superstructures leads to a gap opening in the electronic spectrum. A similar situation is observed in rare earth nickelate perovskites \( \text{RNiO}_3 \). The phase diagram of this family of compounds shows that in most of them there occurs a metal-insulator transition with decreasing temperature, accompanied or driven by the formation of CD, formally 2\( \text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+} \).

Very recently, the double perovskite \( \text{Ca}_2\text{FeMnO}_6 \) was prepared and it has the nominal \( \text{Fe}^{4+} \) and \( \text{Mn}^{4+} \) ions. Again, the \( \text{Fe}^{4+} \) ions are unstable against CD. In the ordered phase of this material, surprisingly the Fe and Mn ions are ordered in alternate layers but not in the common rock salt structure, see Fig. 1. Moreover, this material undergoes a CD transition below 200 K, forming a checkerboard arrangement of the formal \( \text{Fe}^{3+} \) and \( \text{Fe}^{5+} \) ions in each \( \text{FeO}_2 \) layer. As mixed B-site ions may be disordered in perovskites when their ionic sizes are not much different, it is interesting that here the B-site \( \text{Fe}^{4+} \) (0.585 Å) and \( \text{Mn}^{4+} \) (0.530 Å) ions in a similar size are ordered at all, not even to speak about the surprising layered ordering, uncommon in mixed double perovskites. This is the main motivation for us to carry out detailed first principles calculations to address this issue.

As seen below, our results show that this unusual layered ordering facilitates the occurrence of the \( \text{Fe}^{3+}\text{-Fe}^{5+} \) CD of the formal \( \text{Fe}^{4+} \) ions, which however would be frustrated in the standard rock salt structure. In its turn, the \( \text{Fe}^{4+} \) CD tendency actually stabilizes this surprising layered ordering, i.e. these two phenomena are intrinsically interrelated. To substantiate our conclusion, we also carry out a comparative study on the isostructural \( \text{Ca}_2\text{TiMnO}_6 \) with the CD free \( \text{Ti}^{4+} \) and \( \text{Mn}^{4+} \) ions. Our calculations show that \( \text{Ca}_2\text{TiMnO}_6 \) would prefer the common rock salt structure to the layered one. All this demonstrates that the CD is indeed involved in forming the unusual layered ordering of \( \text{Ca}_2\text{FeMnO}_6 \).
FIG. 1. Crystal structure of the double perovskite Ca₂FeMnO₆ with the unusual Fe/Mn layered order.

COMPUTATIONAL DETAILS

The density functional calculations were performed using the full-potential augmented plane wave plus local orbital code (Wien2k). The 2 × 2 × 2 supercell of the ABO₃ perovskite type was set for both the layered structure (see Fig. 1) and rock salt one. The experimental lattice parameters were used and the structural optimization was also carried out. The muffin-tin sphere radii was chosen to be 2.5, 2.0, 2.0 and 1.3 Bohr for Ca, Fe, Mn, and O, respectively. The plane wave expansion of the interstitial wave functionals was set to be 15 Ry. The typical value of Hubbard U=5.0 eV and Hund exchange J=1.0 eV were used for both Fe and Mn 3d states in the LSDA+U calculations to account for the electron correlations. A same set of computational parameters were used in the comparative study of the isostructural Ca₂TiMnO₆.

RESULTS AND DISCUSSION

We started with LSDA+U calculations for the experimental layered structure of Ca₂FeMnO₆. The measured lattice constants were used, and the atomic positions were optimized. To model the observed Fe/Mn layered order and the CD (2Fe⁴⁺ → Fe³⁺ + Fe⁵⁺), we initialized the corresponding density matrix $t_{2g}^{2g}$, $t_{2g}^{3g}$, and $t_{2g}^{4g}$ for Fe³⁺, Fe⁵⁺, and Mn⁴⁺ ions, respectively. All the nearest neighboring magnetic couplings are treated antiferromagnetic. With full electronic and atomic relaxations, we indeed achieved the stable CD solution with layered Fe/Mn ordering and with CD in the Fe layers. This CD solution has two different sets of Fe-O bondlengths, one with the in-plane 2.009 Å × 4 and out-of-plane 1.957 Å × 2, and the other with 1.840 Å × 4 and 1.925 Å × 2. (Note that as the CD occurs in the Fe³⁺ layers of Ca₂FeMnO₆, the in-plane oxygens displace a lot to accommodate the much different planar Fe³⁺-O and Fe⁵⁺-O bonds. However, the out-of-plane oxygens shift much less as their strong covalency with the neighboring Mn⁴⁺ ions, via the $pdσ$ hybridization of the empty Mn⁴⁺ $eg$ orbital, do not allow themselves to move a lot.) The set of longer Fe-O bonds corresponds to Fe³⁺ and the other set of shorter ones to Fe⁵⁺. This assignment is supported by the larger ionic size of Fe³⁺ (0.645 Å) vs the smaller one of Fe⁵⁺ (0.525 Å), and their size difference of 0.12 Å perfectly matches the average bondlength difference between Fe³⁺-O (1.992 Å) and Fe⁵⁺-O (1.868 Å). In addition, these two average bondlengths are very close to those in the CD CaFeO₃ with 1.974 Å for Fe³⁺-O and 1.872 Å for Fe⁵⁺-O. In contrast to the CD Fe ions, the Mn⁴⁺ ions in the layer ordered Ca₂FeMnO₆ have very similar Mn-O average bondlengths: 1.910 Å × 6 (in-plane 1.931 Å × 4 and out-of-plane 1.869 Å × 2) for the Mn⁴⁺ neighboring to the Fe³⁺, and 1.920 Å × 6 (1.913 Å × 4 and 1.935 Å × 2) for the Mn⁴⁺ neighboring to the Fe⁵⁺, see Fig. 1. Moreover, the Fe³⁺ ion has a local spin moment of 4.01 μB within the muffin tin sphere, and Fe⁵⁺ 2.46 μB, see Table I. A certain reduction from their respective formal spin Fe³⁺ S=5/2 and Fe⁵⁺ S=3/2 is due to the strong covalency with the ligand oxygens. Correspondingly, the formal S=3/2 Mn⁴⁺ ion has a reduced spin moment of 2.61 μB.

We plot in Fig. 2 the orbitally resolved density of states (DOS) of Ca₂FeMnO₆. The LSDA+U calculations give an insulating solution for the layered CD state. It can be seen in Fig. 2(a) that the formal Fe³⁺ ion has, as ex-
TABLE I. Relative total energies ∆E (meV/fu) and local spin moments (μB) of the CD layered, the rock salt, and the CD rock salt structures of Ca₂FeMnO₆ calculated by LSDA+U. The CD rock salt structure assumes a Fe⁵⁺-Fe⁵⁺ CD with two different average Fe-O bondlengths adapted from the CD layered structure. The corresponding data for the fully relaxed structures (both the volume and the atomic positions) are listed in the round brackets. The data for the hypothetical Ca₂TiMnO₆ are also included.

| Compound          | ∆E     | Fe⁵⁺ | Fe⁴⁺ | Mn⁴⁺ |
|-------------------|--------|------|------|------|
| CD layered        | 0      | 4.01 | 2.46 | 2.61 |
|                   | (0)    | (3.97)| (2.33)| (2.57) |
| rock salt         | 78     | 3.60 | 2.48 |
|                   | (99)   | (3.50 Fe⁴⁺) | (2.44) |
| CD rock salt      | 221    | 3.89 | 3.03 | 2.50 |
|                   | (260)  | (3.85) | (2.91) | (2.46) |
| Ca₂TiMnO₆         | 0      | 0.00 | 2.68 |
|                   | (0)    | (0.00) | (2.63) |
| rock salt         | −113   | 0.00 | 2.68 |
|                   | (−117) | (0.00) | (2.64) |

FIG. 3. The 3d-orbital DOS of (a) Fe⁴⁺ and (b) Mn⁴⁺, and (c) O 2p DOS of the rock salt structure Ca₂FeMnO₆ by LSDA+U. The blue (red) curves stand for the e₉ (t₂g) state. The positive (negative) value stands for the up (down) spin channel. Fermi level is set at zero energy.

expected for its t₂g e_g S=5/2 configuration, the fully occupied majority-spin t₂g and e_g orbitals, but the minority-spin ones are fully unoccupied. Due to the strong covalency with the ligand oxygens, the lower-energy bonding state at 7 eV below the Fermi level has an even more e_g component than t₂g, although e_g is a higher crystal field level than t₂g. In contrast, the formal Fe⁵⁺ ion has the occupied majority-spin t₂g orbital as seen in Fig. 2(b), but the majority-spin e_g is only partially occupied and this partial occupation is due to the bonding state with the ligand oxygens. Therefore, one could say the Fe⁵⁺ e_g state is formally unoccupied but it gains some occupation due to a very strong covalency with the ligand oxygens as supported by the shortest Fe⁵⁺-O bonds. Moreover, the negative charge transfer character of the unusual high valent Fe⁵⁺ ion favors this strong covalency to form the actual Fe⁵⁺ t₂gⁿ/2 state rather than the nominal Fe⁵⁺ (both the states have the same formal S=3/2). By a comparison between Figs. 2(a) and 2(b), one can see that the formal Fe⁵⁺ has a lower 3d on-site energy (the center of gravity of the 3d DOS) than the Fe⁵⁺, and this is more clear for the unoccupied minority-spin 3d states. This accords with the chemical trend that for a given transition metal, a higher valence state has a lower on-site energy than a lower valence due to an enhanced nuclear attraction in the former. Fig. 2(c) shows that the Mn⁴⁺ ion has a fully occupied majority-spin t₂g orbital but a partial e_g occupation due to a strong covalency of the formally unoccupied e_g orbital with the ligand oxygens as above for the Fe⁵⁺. Therefore, the Mn⁴⁺ ion is in the formal t₂g S=3/2 state. Furthermore, one can see in Fig. 2(d) that the O 2p state has a largest contribution in the topmost valence bands, which reflects the charge transfer character of the insulating gap in this negative charge transfer oxide with an unusual high valence.

Now we turn to the possible rock salt structure of Ca₂FeMnO₆ with a checkerboard arrangement of the Fe and Mn ions, which is a common structure in the B-site ordered double perovskite. In order to make a direct comparison with the above CD layered order, here we use a cubic 2 × 2 × 2 supercell for the rock salt structure with a same lattice volume as above, and the interior atomic positions are relaxed. It is interesting that independent of the initialized Fe⁴⁺-Mn⁴⁺ state or the Fe CD one as done in the LSDA+U calculations for this rock salt structure, both the states converge to an exactly same Fe⁴⁺-Mn⁴⁺ state after a full electronic and atomic relaxation. The Fe⁴⁺-Mn⁴⁺ state in the rock salt structure has a uniform Fe-O bondlength of 1.940 Å ×6, just in between the calculated 1.992 Å for Fe⁵⁺-O and 1.868 Å for Fe⁵⁺-O in the above CD layered structure. The Mn⁴⁺-O bondlength remains almost unchanged, 1.902 Å ×6 here vs 1.910-1.920 Å ×6 in the above CD layered structure. Moreover, the Fe⁴⁺-Mn⁴⁺ state has a local spin moment of 3.60 μB/Fe and 2.48 μB/Mn, which are reduced by a covalency from the formal S=2 for Fe⁴⁺ (t²g e_g) and S=3/2 for Mn⁴⁺ (t²g).

The Fe⁴⁺-Mn⁴⁺ state in the rock salt structure is metallic due to the e_g half filling of the Fe⁴⁺ (t²g e_g) ions, see the DOS results in Fig. 3. This accounts for the uniform Fe⁴⁺ state with an electron itineracy but not a localized Fe⁴⁺-Fe⁵⁺ CD state. These calculations indicate that it is difficult and practically impossible to stabilize the CD phase for the rock salt Fe-Mn ordering (see more discussion below). Indeed, the total energy results show that the Fe⁴⁺-Mn⁴⁺ state in the rock salt structure lies higher in energy than the above CD layered structure by
clear that the Ti$^{4+}$ which has the spin moment of 3.89 can stabilize this state (named CD rock salt in Table I), in Fig. 4. As seen in Table I, our LSDA+U calculation was carried out, this Fe CD in the rock salt structure with the Fe CD. Note that when the atomic relaxation was carried out, this Fe CD in the rock salt structure disappears and evolves into the common rock salt structure with the uniform Fe$^{4+}$-O bonds, which lies higher in energy than the CD layered structure by 78 meV/fu as seen in Table I.

To further confirm that the CD state in the hypothetic rock salt ordered Ca$_2$FeMnO$_6$ is unstable, we constructed a cubic $2 \times 2 \times 2$ supercell with the fixed (here no atomic relaxation) Fe$^{3+}$-O bondlength of 1.992 Å and the Fe$^{3+}$-O one of 1.868 Å (as adapted from the above CD layered structure). This mimics a Fe CD in the Fe-Mn checkerboard structure, and then the Fe$^{3+}$-Fe$^{5+}$ CD ions appear in each Fe-Mn layer, see an illustrative picture in Fig. 4. As seen in Table I, our LSDA+U calculation can stabilize this state (named CD rock salt in Table I), which has the spin moment of 3.89 $\mu_B$ for Fe$^{3+}$, 3.03 $\mu_B$ for Fe$^{5+}$, and 2.50 $\mu_B$ for Mn$^{4+}$. Although this result signals a possible Fe CD in the Fe-Mn checkerboard structure, the corresponding total energy is much higher than the above CD layered structure by 221 meV/fu, once again showing the instability of the rock salt structure with the Fe CD. Note that when the atomic relaxation was carried out, this Fe CD in the rock salt structure disappears and evolves into the common rock salt structure with the uniform Fe$^{4+}$-O bonds, which lies higher in energy than the CD layered structure by 78 meV/fu as reported above (see Table I).

In order to substantiate the above conclusion and to confirm the close relationship between the unusual layered order of Ca$_2$FeMnO$_6$ and the Fe$^{4+}$ CD, here we carry out a comparative study for the isostructural Ca$_2$TiMnO$_6$ but without Fe$^{4+}$ ions leading to CD. We repeated the above calculations as listed in Table I but replaced Fe by Ti free of CD, both of which have a similar ionic size (Ti$^{4+}$ 0.605 Å vs Fe$^{4+}$ 0.585 Å). As seen in Table I, Ca$_2$TiMnO$_6$ has the invariant Ti$^{4+}$ and Mn$^{4+}$ state in both the layered structure and the rock salt one. The Ti$^{4+}$ ion is nonmagnetic and its calculated spin moment is 0, and the Mn$^{4+}$ ion has a local spin moment of 2.68 $\mu_B$ representing its formal S=3/2. It is clear that the Ti$^{4+}$ ions have no CD solution. It is important to note that here the standard rock salt structure of Ca$_2$TiMnO$_6$ is more stable than the layered structure by 113 meV/fu, as seen in Table I. This result is completely opposite to the above one for Ca$_2$FeMnO$_6$, which has the unusual layered order with the Fe CD. Therefore, this comparative study gives another strong indication that the unusual layered ordering of Ca$_2$FeMnO$_6$ is intrinsically connected with the occurrence of the Fe$^{3+}$-Fe$^{5+}$ CD of the formal Fe$^{4+}$ ions in Ca$_2$FeMnO$_6$.

For completeness, and to be sure that we indeed obtained the real ground state of Ca$_2$FeMnO$_6$, we carried out another LSDA+U calculation with a full structural optimization in the layered CD structure. The optimized lattice constants $a$=7.350 Å, $b$=7.390 Å and $c$=7.390 Å (in the $2 \times 2 \times 2$ supercell of the ABO$_3$ perovskite type, see Fig. 1) agree well with the experimental ones ($a$=7.495 Å, $b$=7.489 Å and $c$=7.519 Å) within the typical error bar of ±3% given by density functional calculations. Corresponding calculations were also performed for the rock salt structure and the CD rock salt structure, and the obtained results are summarized in the round brackets in Table I. It is clear that our conclusion is robust and there are only insignificant numerical changes due to the full lattice and atomic relaxations. For example, the local spin moments of the formal Fe$^{3+}$ and Fe$^{5+}$ in the CD layered structure are now 3.97 $\mu_B$ and 2.33 $\mu_B$, respectively (see Table I for a comparison). Moreover, our calculations again find the rock salt structure to be less stable than the CD layered one of Ca$_2$FeMnO$_6$ by 99 meV/fu, and the opposite is true for Ca$_2$TiMnO$_6$. Therefore the above discussion and conclusion remain unchanged: evidently the unusual layered ordering of Ca$_2$FeMnO$_6$ goes hand in hand with the occurrence of the Fe$^{3+}$-Fe$^{5+}$ CD of the formal Fe$^{4+}$ ions which, however would be frustrated in the conventional rock salt structure. Apparently this is responsible for the appearance of this unusual layered ordering in this double perovskite.

**SUMMARY**

All the above calculations prove that the unusual layered order of Ca$_2$FeMnO$_6$ with the Fe CD is the ground state. Why does Ca$_2$FeMnO$_6$ have the unusual layer order rather than a common rock salt structure? This is because Ca$_2$FeMnO$_6$ has the nominal Fe$^{4+}$-Mn$^{4+}$ state. Although Mn$^{4+}$ is stable and has a closed $t_2^6$ subshell, Fe$^{4+}$ ($t_2^6e_g^1$) is an intrinsically unstable high valent Jahn-Teller ion with the formally half filled $e_g$ orbital. The Fe$^{4+}$ ions tend to undergo a CD into Fe$^{3+}$ ($t_2^6e_g^2$) and Fe$^{5+}$ ($t_2^6$) both have a formally closed subshell. In the standard rock salt structure, each Fe$^{4+}$ is surrounded by six Mn$^{4+}$ and vice versa. As a result, the Fe$^{4+}$ ions form a fcc sublattice. If a CD occurs (see Fig. 4), the consequent Fe$^{3+}$ and Fe$^{5+}$ ions would suffer a serious frustra-
tion as in the well known antiferromagnetically coupled fcc lattice (here the two different Fe$^{3+}$ and Fe$^{5+}$ ions behave like the up and down spins in the antiferromagnetic fcc lattice). This should be the reason why the standard rock salt structure does not apply to the B-site ordered Ca$_2$FeMnO$_6$. In contrast, in the unusual layered order of Ca$_2$FeMnO$_6$, the nominal Fe$^{4+}$ and Mn$^{4+}$ ions form their respective layers (which alternate along the a axis, see Fig. 1). Then each Fe$^{3+}$ layer can freely undergo a CD transition and form a planar Fe$^{3+}$-Fe$^{5+}$ checkerboard structure. This CD layered structure turns out to be the ground state as seen above. Therefore, all the above results give us more evidence that the unusual layered ordering of Ca$_2$FeMnO$_6$ is actually intrinsically connected with the tendency of the nominal Fe$^{4+}$ to CD into Fe$^{3+}$ and Fe$^{5+}$.

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