A new type of cathode materials for Li-ion batteries has been explored recently based on FeF₃ in an attempt to raise the energy density and discharge voltage. In this work, the structural and electronic properties of cathode materials FeF₃ for lithium ion batteries have been studied by the first-principles calculations within both the generalized gradient approximation (GGA) and GGA+U frameworks. Our results show that the antiferromagnetic configuration of FeF₃ is more stable than the ferromagnetic one, which is consistent with experiments. An analysis of the electronic density of states shows that FeF₃ is a Mott–Hubbard insulator with a large d–d type band gap. Additionally, a small spin polarization was found on Fe, consistent with a fluorin-mediated superexchange mechanism for the Fe–Fe magnetic interaction.

1. Introduction

Lithium ion batteries (LIBs) have undergone intensive scientific research and shown successful commercial applications in a variety of portable electronic devices, hybrid electric vehicles, and energy storage for renewable energy sources, such as solar and wind. At the present time, the layered intercalation compound LiCoO₂ is utilized as a cathode in most commercial lithium ion batteries. Recently, more developments are based on cathodic insertion materials, such as LiMnO₂, LiNiO₂, and LiFePO₄. The reversible reaction of these insertion materials gives excellent cycling performance but involves at most a single electron transfer per formula unit, corresponding to a limited capacity. What is more, these oxides (e.g., LiMnO₂, LiNiO₂, and LiFePO₄) have safety issues when involved in electrode reaction, because they release oxygen gas at elevated temperatures, which could react with organic solvent exothermally. As opposed to intercalation reactions, the reversible conversion process can utilize all the oxidation states of the transition metal during the redox cycle, which expects to attain a large theoretical energy density. Recently, 3d-transition metal binary compounds MXₙ (M = Co, Fe, Ni, etc.; X = F, O, N, etc.) have been extensively investigated for a large multi-electron redox capacity through reversible electrochemical conversion reactions: MXₙ + nLi⁺ + ne⁻ = yLiₓX + (n−y)M. Of the MXₙ materials, only the metal fluorides can be used as alternative positive electrode materials for LiBs owing to the high operating voltages caused by their ionic character. However, the highly ionic nature of M–F bond leads to a poor electronic conductivity with a wide energy gap. Among transition metal fluorides, iron trifluoride (FeF₃) was selected as a model system because of its low cost and low toxicity. The electrochemical properties of FeF₃ were first investigated by Arai et al. The reported discharge specific capacity of FeF₃ (80 mAh g^{-1}) is far below the theoretical 1e⁻ transfer reaction capacity of the Fe³⁺/Fe²⁺ couple (237 mAh g⁻¹). On the other hand, the fact that electronic/ionic conductivity limitations are no longer insurmountable in the design of high performance electrode materials has led to a renewed interest in the low-cost and abundant Li-based insulating compounds such as phosphates (LiMPO₄), silicates (Li₂SiO₃), borates (LiBO₃), and fluorophosphates (LiMPO₄F). As for FeF₃, the limitation of poor conductivity had been overcome through the use of carbon–metal fluoride nanocomposites (CMFNCs). The CMFNCs also enabled a three-electron reversible process resulting in specific capacities as high as 600 mAh g⁻¹ at 70 °C (note that the theoretical capacity of FeF₃ is 712 mAh g⁻¹), which is the highest energy density value in iron-based cathodes. This performance is roughly four times the specific capacity and nearly three times the gravimetric energy density of LiCoO₂, respectively. It is also found that FeF₃ shows good thermal stability even at elevated temperatures as a cathode for Li-ion batteries. Moreover, iron trifluoride composites (FeF₃–C) prepared by planetary ball milling with carbon showed reversible charge/discharge behavior not only for Li, but also for Na. These previous studies suggest that FeF₃ could be a strong contender as a potential alternative cathode material. Consequently, it is of great interest to explore and understand the intrinsic structural properties and bonding characteristics of the FeF₃ material. In this paper, we focus on the study of ground state properties of FeF₃, by analyzing the structural, magnetic, and electronic properties from first-principles calculations.

2. Computational Method

The present calculations have been performed by using the Vienna ab initio simulation package (VASP), which is based on the density functional theory, the plane-wave basis, and the projector augmented wave (PAW) representation. The exchange-correlation potentials are approximated by the generalized gradient-corrected function (GGA). To take into account the strong correlated character of the d-electrons of iron, a Hubbard-like correction (GGA+U) is included. Within the GGA+U approach, the on-site column term U and the exchange term J can always be grouped together into a single effective interaction parameter U_{eff} = U − J. The exchange parameter J is believed...
to be close to its atomic value $J \approx 1$ eV. The value of $U$ is generally related to the valence state and the structure. Because the calculations on LaFeO$_3$ with the same valence state of Fe and a similar structure (Perovskite) with FeF$_3$ agree with experiment closely when $U$ is set as 6 eV and $U_{eff} = U - J = 5$ eV,$^{24}$ we, therefore, adopt the value of $U$ as 6 eV in the present calculations, which should be a reasonably good approximation. The wave functions were expanded in plane-wave basis up to a kinetic energy cutoff of 500 eV. Brillouin-zone integrations were performed by using special $k$-point sampling of the Monkhorst–Pack scheme$^{25}$ with a $4 \times 4 \times 2$ grid. The convergence of total energy with respect to the kinetic energy cutoff and the $k$-point sampling has been carefully examined. The atomic geometry of FeF$_3$ obtained was fully relaxed until the Hellmann–Feynman forces on all atoms were less than 0.01 eV/Å.

Iron trifluoride was known to show antiferromagnetic (AF) behavior below the Néel temperature of 394 K.$^{26}$ In the corresponding magnetic structure, Fe ions are coupled antiferromagnetically via the intervening F ions to all six nearest neighbor Fe ions. The spin direction had been shown to be parallel to the (111) plane in the bimolecular unit cell,$^{26}$ as shown in Figure 1b. For comparison, in the present work, calculations (collinear) are performed not only for the antiferromagnetic configurations but also for the ferromagnetic (FM) ones. The noncollinear magnetism of FeF$_3$, in the (101) spin direction (which is parallel to the (111) plane), in the AF configuration with the GGA+$U$ method is also calculated. The energy differences between (101) and other spin directions which are also parallel to the (111) plane are all minor. We therefore only present the results in the (101) spin direction.

3. Results and Discussions


Several experimental studies$^{27-29}$ have shown that FeF$_3$ is in a trigonal structure with space group $R3\overline{c}$. The hexagonal representation of the lattice, as shown in Figure 1a, is related to a collapsed ReO$_3$ perovskite structure. The Fe$^2+$–Fe bond angle has deviated from the ideal $180^\circ$ (experimental value of $153^\circ$ $^{27}$). FeF$_3$ has a layer structure and comprises corner-sharing FeF$_6/2$ octahedra. In this structure, planes of Fe atoms and planes of fluorine atoms, perpendicular to the [001] direction, lie alternately and regularly. The fluorine atoms arrangement in FeF$_3$ may be regarded as a considerably distorted hexagonal close-packing. In addition, it is notable to remark that the Fe$^{3+}$ ions, which are in the center of a regular octahedron of equidistant fluorine, lie on the (012) planes of the trigonal structure. It is reasonable to expect that the (024) vacant plane between Fe (012) planes is available for Li$^+$ insertion.

In Table 1, we present the calculated lattice parameters, the bond length of Fe–F, the bond angle of Fe–F–Fe, and the spin magnetic moments of Fe and F ions in FeF$_3$. Both of our GGA and GGA+$U$ calculations predict that the AF configuration is more stable than the FM one. The differences of cohesive energies (per molecular formula) between AF and FM configurations are 0.291 eV for GGA and 0.130 eV for GGA+$U$ calculations. It is noted that the optimized lattice parameters for AF configuration are in good agreement with experiment results$^{27}$ (with an error less than 2%). Overall, our GGA+$U$ calculations slightly overestimate the equilibrium unit cell volume with an error of 3.8%. Such an overestimation is in line with that found in the common GGA calculations. As we can see, the calculated Fe–F bond lengths show slight overestimation with respect to experimental data to within 1.0% for the AF and GGA+$U$ calculations. The structure of FeF$_3$ is related to a collapsed ReO$_3$ perovskite structure, and the distortion of the ReO$_3$ perovskite structure can be considered as a tilting of the rigid FeF$_6/2$ octahedron. To better understand the distorted structures, the bimolecular unit cell of FeF$_3$ is shown in Figure 1b. Such a rhombohedrally distorted structure can be characterized by three parameters: (1) the octahedral tilt angle $w$, which denotes the rigid rotation of a FeF$_6/2$ octahedron; (2) the change of unit cell volume; and (3) a $c/a$ ratio, with $c$ and $a$ shown in the Figure 1b. For the present FeF$_3$ with an AF configuration, the octahedral tilt angle is $w = 12.9^\circ$, which is obtained from the bond angle of Fe–F–Fe, i.e., $(180^\circ - 154.2^\circ)/2 = 12.9^\circ$. Due to the octahedral tilt, the unit cell volume shrinks, leading to a decrease in the volume of $\Delta V/V = -6.88\%$ and an increase of ratio $c/a = 1.027$. Both values are very close to the calculated values of $\Delta V/V = -\sin^2 w = -5\%$ and $c/a = 1/cos w = 1.026$, respectively.

3.2. Electronic and Magnetic Properties.

The band structure of FeF$_3$, together with the corresponding total density of states (TDOS), in the antiferromagnetic configuration calculated by the GGA+$U$ scheme has been shown in Figure 2. To comprehend the electronic properties more clearly, the $l$-decomposed and projection over atomic contributions of the density of states for FeF$_3$ predicted by GGA and GGA+$U$ methods are also calculated for both the FM and AF configurations, and the data are presented in Figure 3 for comparison. By considering data outlined in Figure 3d, we can interpret the band structure and the sequence of partial DOS peaks appearing from low to high energies as follows. The band structure is shown to be divided into several regions. Two narrow bands located at around −7 and −6 eV, corresponding to two sharp peaks in the DOS plot (Figure 3d), are of mainly Fe-3d character and with small F-2p contributions. In the energy region from −4.5 eV to the top of the valence band, according to the DOS plot in Figure 3, the bands show significant admixture of fluorine 2p and iron 3d states (i.e., showing a significant hybridization of F-2p and Fe-3d atomic orbitals). For the conduction band located at energy larger than 4 eV, the contribution is almost fully from the Fe-3d orbit (Figure 3d). Figure 3a–d suggests that the electronic structures predicted by the GGA+$U$ method are quite different from those by the GGA scheme. The GGA calculations predicted FeF$_3$ to be a semiconductor with band gaps of 0.267 eV for FM and 1.800 eV for AF, respectively, while GGA+$U$ calculations indicated that FeF$_3$ is an insulator with band gaps of 3.019 eV for FM and 4.138 eV for AF configurations, respectively. As the valence conduction band gap separates Fe-d states, FeF$_3$ is a classic Mott–Hubbard
insulator like FeF$_2$, rather than a charge-transfer insulator such as Fe$_2$O$_3$. It is reported that the energy gap in FeF$_3$ thin films is about 5.96 eV, which suggests that the present AF calculations is a better prediction of the band gap than FM ones. This is reasonable when taking into account the strong correlated character of the Fe d-electrons. The wide energy gap resulting in poor electronic conductivity seems likely to restrict the application of FeF$_3$ as rechargeable cathode materials. However, electronic limitations are no longer an insurmountable issue in the design of high-performance electrode material. It can be overcome through various materials processing approaches, including the use of carbon coatings, mechanical grinding, or mixing, and low-temperature synthesis routes to obtain tailored particles. Therefore, low-cost and abundant Li-based insulating compounds, such as FeF$_3$, have gained renewed interests in order to obtain high voltage and large capacity. From Figure 3, it is also shown that antiferromagnetic DOS’s are much more localized than those of ferromagnetic ones (i.e., the band structures of AF FeF$_3$ are much more localized than those of FM FeF$_3$, for both the GGA and GGA+$U$ calculations).

For all the FM and AF calculations, Fe ions are found to have high-spin ground states with the up-spin Fe-3d bands completely filled while the down-spin Fe-3d bands are nearly unoccupied. The calculated magnetic moments of Fe, as shown in Table 1, are all close to the experimental value of 4.528 µB, which are also quite near the saturation value of 5 µB according to Hund’s rule. We have also performed calculations on the noncollinear magnetism of FeF$_3$ in the AF configuration with the GGA+$U$ method. The magnetic moment from noncollinear magnetism calculation is 4.445 µB, while the magnetic moment is 4.367 µB for the collinear magnetism calculations. The spin configuration of Fe-ions in the material is vital to the bond angle of Fe–F–Fe in the structure. The high-spin configuration of Fe$^{3+}$ (3d$^5$ in t$_{2g}^3$e$_g^2$) with three holes in the t$_{2g}$ shell contributes to the distorted structure of FeF$_3$ due to the PJT coupling (pseudo Jahn–Teller effect) between the empty 3d orbit of Fe and the full 2p orbit of the F.

The deformation charge density plot for the plane containing the Fe–F–Fe bond of FeF$_3$ is shown in Figure 4a. The deformation charge density, $\Delta F(r_b)$, is defined as the difference between the total charge density in the solid and the superposition of the charge density of the isolated atoms. The difference of cohesive energies per molecular formula for the noncollinear and collinear magnetism is 0.002 eV, while the collinear calculation turns out to be a little bit more stable than the collinear calculation. The spin configuration of Fe-ions in the material is vital to the bond angle of Fe–F–Fe in the structure.

### Table 1: The Optimized Lattice Parameters, the Fe–F Bond Length, the Bond Angle of Fe–F–Fe, and the Magnetic Moments of Fe and F Ions of FeF$_3$

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$, Å</th>
<th>$c$, Å</th>
<th>V, Å$^3$</th>
<th>$R_{	ext{Fe–F}}$, Å (error)</th>
<th>$\angle_{	ext{Fe–F–Fe}}$, deg</th>
<th>$m$(Fe), µB</th>
<th>$m$(F), µB</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF: Exp 31</td>
<td>5.198</td>
<td>13.331</td>
<td>311.93</td>
<td>1.92</td>
<td>153</td>
<td>4.528</td>
<td></td>
</tr>
<tr>
<td>FM: GGA</td>
<td>5.199</td>
<td>13.573</td>
<td>317.52</td>
<td>1.959 (2.0%)</td>
<td>147.2</td>
<td>4.230</td>
<td>0.216</td>
</tr>
<tr>
<td>FM: GGA+$U$</td>
<td>5.177</td>
<td>13.484</td>
<td>312.84</td>
<td>1.946 (1.4%)</td>
<td>147.9</td>
<td>4.445</td>
<td>0.146</td>
</tr>
<tr>
<td>AF: GGA</td>
<td>5.278</td>
<td>13.495</td>
<td>325.44</td>
<td>1.943 (1.2%)</td>
<td>154.2</td>
<td>4.047</td>
<td>0</td>
</tr>
<tr>
<td>AF: GGA+$U$</td>
<td>5.277</td>
<td>13.430</td>
<td>323.90</td>
<td>1.939 (1.0%)</td>
<td>154.2</td>
<td>4.367</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 2. Band structure and the corresponding total density of states (TDOS) for FeF$_3$ in the antiferromagnetic configuration from GGA+$U$ calculations. As for DOS, only the spin-up results are given. The Fermi level is at zero energy.

Figure 3. The density of states for FeF$_3$ predicted by GGA and GGA+$U$ methods for ferromagnetic and antiferromagnetic states, respectively. The positive (negative) value is for the majority (minority) spin contribution. The total DOS and the Fe-3d and F-2p partial DOS’s are presented by black, red, and blue lines, respectively. The Fermi level is at zero energy.
tion of independent atomic charge densities placed at the atomic sites of the same solid, i.e.,

\[ \Delta \rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum \rho_{\text{atoms}}(\mathbf{r} - \mathbf{R}_\mu) \]

where \( \mathbf{R}_\mu \) is the atomic coordinate. For the present deformation charge densities, all the calculated results give similar maps. Therefore, only the result from the GGA+U approach in the AF configuration is presented in Figure 4a. According to Figure 4a, the bonding between Fe and F shows both conspicuous ionic characteristic and slight covalency, in line with the high electronegativity of the F atom. This is confirmed by the covalency analysis in which covalency of the Fe–F bonds in FeF₃ was indicated to be quite low compared with that of a similar oxide environment for Fe₃⁺.³³ Remarkable charge polarization of F ion is also found, which is a consequence of interactions between the neighboring F–Fe ions. The anion polarizability and dipole–dipole interactions³⁵ have been proved as the major influences about the stabilization of tilts of corner-coupled rigid octahedral.

To further understand the magnetic properties, the calculated spin density plots (spin-up minus spin-down) for the AF configuration within the GGA+U scheme are given in Figure 4b. The magnetism of FeF₃ is mainly expressed by Fe as expected. Fe shows remarkable high-spin magnetism correlated to the spin polarization is clearly visible in Figure 4b. This is because Fe₁ repulses spin-down electrons but attracts spin-up ones of Fe, leaving an excess of spin-down electrons on F in the direction of Fe₁–F. The opposite occurs in the Fe₂–F case. A similar effect of spin electrons transfer was discussed before for FeF₂³² and Fe₂O₃.³³ The spin polarization on F is convincing evidence that conforms to the Fe₁–Fe₂ superexchange interaction via the diamagnetic ligand F.

4. Conclusion

In summary, first-principles calculations based on the density functional theory and the GGA and GGA+U schemes have been used to predict the structural properties and electronic structures of FeF₃ in the ferromagnetic and antiferromagnetic states. Our results show that GGA+U approximation provided more reasonable predictions on the structural and electronic properties of FeF₃, considering the strongly correlated 3d electrons of Fe. The optimized structural parameters of antiferromagnetic FeF₃ from GGA+U are 1–2% in excess in comparison with the experimental ones. By comparing the cohesive energies of FeF₃ in the AF and FM states, the antiferromagnetic FeF₃ also turns out to be more stable, consistent with experiments. The electronic structure calculations indicate that FeF₃ is a Mott–Hubbard insulator with strong ionic character and a large bandgap (with then a poor conductivity). Actually, the limitation of poor conductivity has been overcome through the use of carbon–metal fluoride nanocomposites. Further theoretical and experiment work on the doping of transitional metal ions to acquire better conductivity and phase stability should also be helpful. Furthermore, the structure analysis on the layered structure of FeF₃ in this paper provides some useful insights into the understanding of the Li insertion properties (Li,FeF₃) as well as the lithium migration.

Acknowledgment. The present work is supported by the National Natural Science Foundation of China (Grant No.10774124) and the National 973 Program of China (Grant No. 2007CB209702).

References and Notes

Properties of Li-Ion Battery Cathode Material FeF₃


JP1050518