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Structural and electronic properties of Li-ion battery cathode material MoF₃ from first-principles

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ABSTRACT

The transition metal fluorides have been extensively investigated recently as the electrode materials with high working voltage and large capacity. The structural, electronic and magnetic properties of MoF₃ are 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 MoF₃ is more stable than the ferromagnetic one, which is consistent with experimental results. The analysis of the electronic density of states shows that MoF₃ is a Mott–Hubbard insulator with a *d*–*d* type band gap, which is similar to the case of FeF₃. Moreover, small spin polarizations were found on the sites of fluorine ions, which accords with a fluorine-mediated superexchange mechanism for the Mo–Mo magnetic interaction.

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1. Introduction

Lithium-ion batteries (LIBs) have undergone widely scientific research and shown successful commercial applications in a variety of portable electronic devices and electric vehicles [1,2]. At present, LiCoO₂ is utilized as a cathode in most of the commercial lithium ion batteries [3,4], however, the active reversible specific capacity of LiCoO₂ is below 150 mA h g⁻¹ which cannot well meet the requirement of the power lithium ion battery. To satisfy the demand for the electric vehicles, much attention has been paid to the development of new systems, in particular to those with high energy density and discharge voltage which can store more energy at reduced weight [5–11]. In a way, the choice of cathode materials is very important. Good cathode material can accommodate a large amount of Li-ions, which can supply high capacity. Recently, as a special class of promising cathode materials, transition metal fluorides have attracted great interest due to high ionicity which can provide high operating voltage in Li-ion batteries [12–15]. Metal fluorides enable the highest specific capacity via the large multi-electron reversible

redox conversion process through the following reaction scheme:



However, the highly ionic nature of M–F bond leads to an insulating character of MF with poor electronic conductivity and limits their discharge voltage. For example, the discharge capacity of FeF₃ (80 mA h g⁻¹) first reported by Arai et al. [16] is far below the theoretical 1e⁻ transfer reaction capacity of the Fe³⁺/Fe²⁺ couple (237 mA h g⁻¹). Fortunately, electronic limitations are no longer an insurmountable issue in design of high-performance electrode material. Low conductivity can be improved through various materials processing approaches, including the use of carbon coatings, mechanical grinding, mixing [17], and low-temperature synthesis routes [14] to obtain tailored particles. Among transition metal fluorides, FeF₃, CuF₂ [18] are widely investigated, however, little has been done on MoF₃. As is well known, molybdenum is a multi-valence-electron element which could enable a six-electron reversible process resulting in specific high capacities. Therefore, element Mo has been very active in the field of lithium ion batteries. Molybdenum disulfide and molybdenum oxide are well-known lithium insertion compounds and have been much investigated [19,20]. Moreover, experiments [21] have shown that MoF₃ and FeF₃ have the same crystal structure and magnetic structure. The magnetic ground state of MoF₃ or FeF₃ is antiferromagnetism (AFM), in which each metal atom is antiferromagnetically coupled through the intervening fluorine atoms to each of its six nearest neighbors. Consequently, it is of great interest to explore and understand the intrinsic structural properties and electronic characteristics of

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the MoF₃ material. In this paper, we focus on the study of ground state properties of MoF₃, by analyzing the structural, magnetic, and electronic properties from first-principles calculations.

The present calculations have been performed by using the Vienna ab initio simulation package (VASP) [22,23], which is based on the density functional theory, the plane-wave basis, and the projector augmented wave (PAW) representation [24]. The exchange correlation potentials are approximated by the generalized gradient-corrected approximation (GGA) [25]. To address the on-site Coulomb interactions in the localized *d* electrons of Mo ions, the GGA+U method with an additional Hubbard-type U term [26] was employed. Here, an $U_{\text{eff}}=U-J=2$ eV is used in this paper. In the study of magnetism of MoO₂, Wang et al. [27] used a range of values for U_{eff} between 1 and -1 eV, citing weak correlations in Mo. Jain and Hautier [28] more accurately predicted the formation enthalpies of 49 ternary oxides by mixing GGA and GGA+U energies, they arrived at a value of $U_{\text{eff}}=3.5$ for Mo. Saitoh et al. [29] suggested a value of $U_{\text{eff}}=1.0$ for Mo based on a comparison of the computed band structure with valence-band photoemission spectra of single crystals of Sr₂FeMoO₆. We, therefore, take an average value of $U_{\text{eff}}=2.0$ eV. 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 [30] 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 examined. The atomic geometry of MoF₃ was fully relaxed until the Hellmann–Feynman forces on all atoms were less than 0.01 eV \AA^{-1} . The unit cell adopted for the present calculation contains 6 formula unit of MoF₃, which is 24 atom per unit cell (18 fluorine atoms and 6 Mo atoms).

Several experimental studies [21,31] have shown that MoF₃ has a bimolecular rhombohedral unit cell of space group $R\bar{3}c$. The hexagonal representation of the lattice, as shown in Fig. 1, is related to a collapsed ReO₃ perovskite structure. The Mo–F–Mo bond angle is deviated from the ideal 180° (experimental value of 141.02° [31]). MoF₃ also exhibits a layered structure and comprises corner-sharing MoF_{6/2} octahedra. In Table 1, we have presented the calculated lattice parameters, the bond length of Mo–F, the bond angle of Mo–F–Mo and the spin magnetic moments of Mo and F ions in MoF₃. Both of the GGA and GGA+U calculations predict that the AFM configuration is more favorable. The differences of cohesive energies (per molecular formula) between antiferromagnetic and ferromagnetic configurations are 0.476 eV for GGA and 0.234 eV for GGA+U calculations, respectively. Their lattice parameters calculated within the GGA+U scheme are larger than those calculated within the GGA.

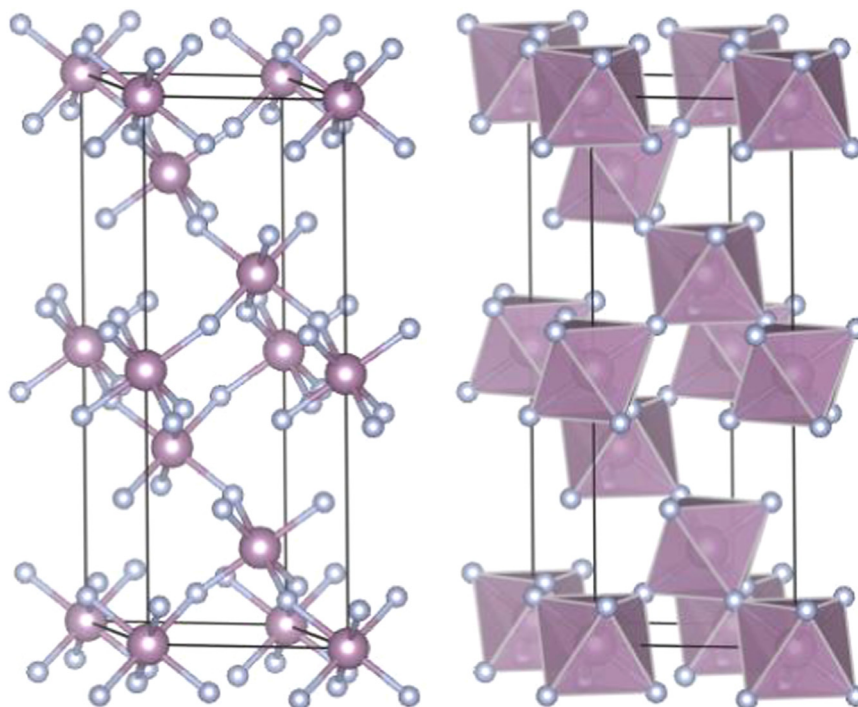


Fig. 1. The crystal structure of MoF₃ in the hexagonal structure. The Mo and F atoms are denoted by larger and smaller balls, respectively. Mo–F₆ octahedra are also shown in the right panel.

Table 1
The optimized lattice parameters, the cohesive energies E_c (in eV/molecular formula), the Mo–F bond lengths, the bond angles of Mo–F–Mo, and the magnetic moments of Mo and F ions of MoF₃ for the FM and AFM configurations calculated by both the GGA and GGA+U schemes, together with the experimental data [31].

Method	a (Å)	c (Å)	E_c (eV)	$R_{\text{Mo-F}}$ (error) (Å)	$\angle\text{Mo-F-Mo}$ (°)	m (Mo) (μB)	m (F) (μB)
AFM [31]	5.213	14.41	–	2.04	141.02		
FM: GGA	5.276	14.492	152.098	2.07 (1.4%)	139.37	2.689	0.054
FM: GGA+U	5.410	14.782	145.350	2.08 (1.9%)	139.80	3.053	0.021
AFM: GGA	5.388	14.395	152.574	2.06 (0.9%)	145.10	2.513	0
AFM: GGA+U	5.386	14.557	145.584	2.08 (1.9%)	143.16	2.721	0

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