Antiferromagnetism of Double Molybdate LiFe(MoO₄)₂

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ABSTRACT: The magnetic properties of the spin-5/2 double molybdate LiFe(MoO₄)₂ have been characterized by heat capacity, magnetic susceptibility, and neutron powder diffraction techniques. Unlike the multiferroic system LiFe(WO₄)₂ which exhibits two successive magnetic transitions, LiFe(MoO₄)₂ undergoes only one antiferromagnetic transition at T_N ~ 23.8 K. Its antiferromagnetic magnetic structure with the commensurate propagation vector k = (0, 0.5, 0) has been determined. Density functional theory calculations confirm the antiferromagnetic ground state and provide a numerical estimate of the relevant exchange coupling constants.

I. INTRODUCTION

Double tungstates and molybdates with the chemical formula A'B₃(VO₄)₂ form a big family of transition metal oxides, where A is an alkali metal, B is a trivalent cation such as Bi³⁺, In³⁺, or Fe³⁺ or a rare earth, Sm³⁺ or Eu³⁺; and M represents W⁶⁺ or Mo⁶⁺. The combinations of three categories of metal ions make this family full of varieties in physics and functionality. The inclusion of the Li ion at A site makes these materials, while the W/Mo can provide a relative large spin orbit coupling considering its 4d/5d orbitals. Most importantly, the B-site ions with narrow bands can provide other applicable physical properties, such as magnetism and luminescence.

Recently, NaFe(WO₄)₂ was reported to exhibit an incommensurate spiral spin order at low temperature (<4 K), although this magnetism can not induce a net ferroelectric (FE) polarization (P) due to the opposite chirality coexisting in this material. Differently, Liu et al. revealed a more interesting magnetic spiral in LiFe(WO₄)₂, which breaks the spatial reversal symmetry and induces a net FE P along the [010] axis below 19.7 K through the inverse Dzyaloshinskii–Moriya (DM) interaction. Thus, LiFe(WO₄)₂ is the second experimentally confirmed multiferroic material in the tungstate family, following the first one MnWO₄. Despite the common chemical formula, the crystalline structures of double tungstates/molybdates can vary in a large range. In fact, LiFe(WO₄)₂ and NaFe(WO₄)₂ are different in their space groups (C2/c vs P2/m), and the arrangements of Fe ions are distinct. Such structural diversity makes it possible to find more exotic magnetic properties in double tungstates/molybdates. For instance, it was reported that RbFe(MoO₄)₂ possesses a noncollinear magnetic order below 3.8 K which can trigger the ferroelectricity. In addition, there are lots of other tungstates/molybdates members, e.g., FeWO₄, CoWO₄, NiWO₄, CuWO₄, α-FeMoO₄, α-CoMoO₄, and NaCr(WO₄)₂, all of which display collinear antiferromagnetic orders and thus are not ferroelectric. Recently, Chen et al. synthesized LiFe(MoO₄)₂ and investigated it for its applications in lithium-ion batteries. Distinct from either LiFe(WO₄)₂ or NaFe(WO₄)₂, LiFe(MoO₄)₂ possesses a new space group P1 and another type of Fe framework. Its excellent electrochemical properties have been carefully studied. Nevertheless, its magnetic properties have never been studied yet.

In this work, we will report the magnetism of LiFe(MoO₄)₂ determined from combined studies of heat capacity, magnetic susceptibility, neutron powder diffraction, as well as density functional theory (DFT) calculation. An antiferromagnetic (AFM) phase transition is found around 23.8 K. Below the Neel temperature (T_N), a long-range magnetic ordering is established with a commensurate propagation vector (0, 0.5, 0), which does not yield multiferroicity. Above T_N, short-range magnetic correlation persists, leading to considerable magnetic entropy.

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II. METHODS

High-quality polycrystalline LiFe(MoO$_4$)$_2$ samples were synthesized using the conventional solid state reaction method in air, with the highly purified powder of oxides and carbonates as starting materials. The stoichiometric mixtures were ground and fired at 550 °C for 24 h in air. The resultant powder was reground and pelleted under a pressure of 1000 psi into disks of 2.0 cm in diameter, and then, these pellets were sintered at 650 °C for 24 h in air again. Phase purity of the sample was checked using X-ray diffraction (XRD) with the Cu Kα radiation at room temperature. The magnetic properties were measured using a superconducting quantum interference device magnetometer (SQUID) equipped on a quantum design magnetometer (MPMSXL-7). The specific heat was measured on the physical property measurement system (PPMS, Quantum Design) using the heat relaxation method. Neutron powder diffraction (NPD) patterns were collected with neutron wavelength $\lambda = 2.41$ Å at the HB-2A powder diffractometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory.

DFT calculations were performed using the Vienna ab initio simulation package (VASP) with the projector augmented-wave (PAW) potentials.$^{26-28}$ The Perdew–Burke–Emzerhof for solids (PBEsol) exchange function has been adopted$^{29}$ to obtain an accurate description of the crystal structure of LiFe(MoO$_4$)$_2$. The Hubbard $U_{\text{eff}}$ ($= U - J$) was imposed on Fe's d orbitals using the Dudarev implementation$^{30}$ considering the strong correlation effect of 3d orbitals. No $U_{\text{eff}}$ is applied to Mo's 4d orbitals considering its empty magnetic unit cell. Besides, both the lattice constants and atomic positions were fully relaxed until the Hellmann–Feynman force on each atom is below 0.01 eV/Å.

III. RESULTS AND DISCUSSION

Figure 1a shows the crystal structure of LiFe(MoO$_4$)$_2$, which is described in the triclinic space group $P\overline{1}$ (No. 2) and consists of separated layers of [LiO$_6$] monocapped trigonal bipyramids, [FeO$_6$] octahedra, and [MoO$_4$] tetrahedra. The framework of magnetic Fe ions in LiFe(MoO$_4$)$_2$ is shown in Figure 1b.

Figure 1c shows the powder XRD pattern of LiFe(MoO$_4$)$_2$ at room temperature. The lattice parameters were refined using the space group $P\overline{1}$ with the Rietveld refinement technique. No impurity phase is observed in the XRD power pattern. The refined lattice parameters of LiFe(MoO$_4$)$_2$ are $a = 6.7766$ Å, $b = 7.1679$ Å, $c = 7.3104$ Å, $\alpha = 90.89^\circ$, $\beta = 110.38^\circ$, and $\gamma = 105.21^\circ$, which are in good consistency with previous works.$^{31,32}$

Besides XRD, NPD data of LiFe(MoO$_4$)$_2$ were collected at $T = 40$ K, as shown in Figure 1d. The nuclear structure refinement was conducted using FullProf with the Rietveld method.$^{26}$ Our refinement confirms that the compound possesses a triclinic structure with the space group $P\overline{1}$. No impurity phase was detected. The corresponding lattice parameters are $a = 6.751(1)$ Å, $b = 7.203(2)$ Å, $c = 7.1702(1)$ Å, $\alpha = 90.6739(17)^\circ$, $\beta = 110.2274(14)^\circ$, and $\gamma = 105.5793(17)^\circ$, in agreement with above XRD results. Table 1 summarizes more parameters such as atomic coordinates and displacement parameters.

Figure 2a depicts the magnetic susceptibility ($\chi$) and its inverse ($1/\chi$) as a function of temperature ($T$) measured following zero field cooling (ZFC) and field cooling (FC) processes at a 0.1 T field. The two curves almost overlap, and no bifurcation is seen in the whole temperature range, suggesting the absence of glass behavior. A peak of $d\chi/dT$ was observed around $T_N \sim 23.8$ K, indicating the establishment of long-range magnetic ordering, as shown in the inset of Figure 2b. The $\chi(T)$ of LiFe(MoO$_4$)$_2$ can be well fitted to the Curie–Weiss law $\chi = C/(T - \theta_{\text{CW}})$, as also shown in Figure 2a. Our fitting in the temperature range between 100 and 300 K yields the Curie constant $C \sim 4.53$ emu K/mol and negative Curie–Weiss temperature $\theta_{\text{CW}} \sim -52.85$ K, suggesting dominant AFM interactions between Fe's spins. The effective moment per Fe$^{3+}$ of 6.02 $\mu_B$ is very close to spin-only moment (5.92 $\mu_B$) for high-spin Fe$^{3+}$ ($S = 5/2, L = 0$).

Figure 2b shows the magnetic susceptibility under a high magnetic field (6 T). There is a maximum of $\chi$ at $T_{\text{max}} \sim 32.8$ K, which may due to the ordering of short-range magnetic

![Figure 1.](image_url)
In addition, Figure 2c shows the magnetization ($M$) as a function of temperature acquired by subtracting the phonon contribution using nonmagnetic LiGa(MoO$_4$)$_2$ (left $y$-axis) and the magnetic entropy $S_{mag}$ as a function of temperature (right $y$-axis).

Figure 3. (a) Heat capacity of magnetic LiFe(MoO$_4$)$_2$ and nonmagnetic LiGa(MoO$_4$)$_2$ measured under 0 T magnetic field. (b) Magnetic contribution of the specific heat $C_{mag}$ as a function of temperature by subtracting the phonon contribution using nonmagnetic LiGa(MoO$_4$)$_2$ (left $y$-axis) and the magnetic entropy $S_{mag}$ as a function of temperature (right $y$-axis).

Figure 2. (a) Temperature dependence of magnetic susceptibility (left $y$-axis) and its inverse (right $y$-axis) of LiFe(MoO$_4$)$_2$ measured under 0.1 T field. (b) Temperature evolution of magnetic susceptibility under various magnetic fields. The inset shows the amplified view of the derivative of $\chi$ around the phase transition temperature. (c) Moment size of the Fe$^{3+}$ ion as a function of magnetic field at various temperatures.
reproduce the correct magnetic intensities, the $\Gamma_2$ spin model gives us good fitting results as shown in Figure 4b. The corresponding magnetic structure is presented in Figure 5 with the refined amplitude of the magnetic moment $4.23(1) \mu_B$. The projections of the moment on the crystallographic axes are $(m_x, m_y, m_z) = (0.582, 4.2, 1.296) \mu_B$. This value is only slightly smaller than the expected value for the spin $S = 5/2$, but it is still reasonable considering the low-dimensionality magnetic interactions.

To further understand the magnetic properties, DFT calculations have been performed. Various possible magnetic arrangements were checked, such as ferromagnetic (FM), AF1–AFM, AF2–AFM, and AF3–AFM, as shown in Figure 6. As shown in Figure 7, the AF2–AFM configuration has the lowest energy despite the choice of $U_{eff}$, in agreement with our neutron experimental result. The calculated local magnetic moment of the AF2–AFM state is $4.22 \mu_B$ at $U_{eff} = 4$ eV, which is quite close to our neutron experiments ($4.23 \mu_B$).

In fact, $U_{eff} = 4$ eV is a proper choice to describe Fe’s 3d orbitals according to previous studies, which will be adopted as the default one. The optimized lattice constants of the AF2–AFM state are $a = 6.748$ Å, $b = 7.233$ Å, and $c = 7.113$ Å, which are quite close to our neutron experiments ($a = 6.751$ Å, $b = 7.203$ Å, $c = 7.1702$ Å at 1.5 K).

Furthermore, the magnetism of LiFe(MoO$_4$)$_2$ can be described using a Heisenberg model:

$$H = -J_1 \sum_{\langle ij \rangle} S_i S_j - J_2 \sum_{\langle ii \rangle} S_i S'_i - J_3 \sum_{\langle m n \rangle} S_m S_n$$

(1)

where $J_1$, $J_2$, and $J_3$ are the exchange couplings (as indicated in Figure 1b) between iron spins $S$'s. Using the optimized ground state configuration, the exchange coefficients are extracted from DFT calculations: $J_1 = -18.03$ meV, $J_2 = 2.06$ meV, and $J_3 = 2.07$ meV, respectively. The strongest negative exchange $J_1$ indicates the AFM coupling between the nearest neighbor iron spins. Those longer distance exchanges $J_2$ and $J_3$ are much smaller.
weaker: the positive $J_2$ implies FM interaction along the $b$-axis, and the positive $J_3$ means that the magnetic coupling between near iron is FM exchange. In short, our theoretical calculation confirms the magnetic ground state of LiFe(MoO$_4$)$_2$.

The atomic-projected density of states (DOS) of the AF2−AFM state is shown in Figure 8. It is clear that this system is an insulator with an indirect gap of 2.46 eV. According to DOS, the topmost valence bands are mainly contributed by the hybrid O’s 3p orbitals and Fe’s 3d orbitals (lower Hubbard bands), while the lowest conduction bands are mainly from Fe’s 3d orbitals (i.e., upper Hubbard bands). The slight reduction of local magnetic moment from the ideal 5 $\mu_B$/Fe is due to such hybridization.

IV. CONCLUSION

In summary, the physical properties of the spin-5/2 double molybdate LiFe(MoO$_4$)$_2$ have been systematically investigated experimentally and theoretically. Our magnetic susceptibility and heat capacity measurements found an antiferromagnetic long-range ordering at $T_N \sim 23.8$ K, which was further confirmed by neutron diffraction. Its antiferromagnetic magnetic structure with the commensurate propagation vector $k = (0, 0.5, 0)$ has also been determined. Our DFT calculations further verified the magnetic ground state. Short-range magnetic correlation was also made evident above the Néel temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00432.

- Powder diffraction data table (PDF)
- Magnetic structure file of LiFe(MoO$_4$)$_2$ (MCIF)

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Notes

The authors declare no competing financial interest.
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