2007

Magnetic anisotropy in doped and undoped LiFePO₄ single crystals

Dapeng Chen

University of Wollongong, dapeng@uow.edu.au

Xiaolin Wang

University of Wollongong, xiaolin@uow.edu.au

Y S Hu

Max Planck Institute for Solid State Research

C T Lin

Max Planck Institute for Solid State Research

S. X. Dou

University of Wollongong, shi@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>

Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/3207>

Recommended Citation

Chen, Dapeng; Wang, Xiaolin; Hu, Y S; Lin, C T; Dou, S. X.; and Nigam, Rashmi: Magnetic anisotropy in doped and undoped LiFePO₄ single crystals 2007, 09N512-1-09N512-3.
<https://ro.uow.edu.au/engpapers/3207>

Authors

Dapeng Chen, Xiaolin Wang, Y S Hu, C T Lin, S. X. Dou, and Rashmi Nigam

Magnetic anisotropy in doped and undoped LiFePO_4 single crystals

D. P. Chen and Xiaolin Wang^{a)}

*Institute for Superconducting and Electronic Materials, University of Wollongong,
New South Wales 2522, Australia*

Y. S. Hu and C. T. Lin

*Max Planck Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart,
Federal Republic of Germany*

S. X. Dou and R. Nigam

*Institute for Superconducting and Electronic Materials, University of Wollongong,
New South Wales 2522, Australia*

(Presented on 11 January 2007; received 29 October 2006; accepted 21 December 2006;
published online 3 May 2007)

We report on the magnetic anisotropic properties of pure and Mg doped LiFePO_4 single crystals grown by the traveling solvent floating zone technique. Our results reveal a considerable anisotropy in the susceptibilities along $H\parallel a$, $H\parallel b$, and $H\parallel c$ for both crystals. LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ crystals show antiferromagnetic long-range ordering below the Néel temperature of about 52 K, with the b axis being the magnetic easy axis. The effective moments have been determined to be $6.18\mu_B$ and $6.07\mu_B$ for the pure and the doped crystals, respectively. These values are higher than what is expected on the basis of the spin-only value of $6.70\mu_B$ with a high-spin d^6 configuration for the Fe^{2+} ion. © 2007 American Institute of Physics. [DOI: [10.1063/1.2712326](https://doi.org/10.1063/1.2712326)]

I. INTRODUCTION

Olivine phosphate materials have potential practical importance as cathode materials to be used in rechargeable lithium-ion batteries. In this family of compounds, lithium iron phosphate, LiFePO_4 (LFPO), provides an attractive voltage of 3.5 V, high theoretical capacity, low cost, ease of synthesis, and stability when used with common organic electrolyte systems. It has become one of the most promising candidates for this application.^{1,2} However, from the viewpoints of both fundamental and practical research, a significant controversy exists concerning the origin of the low intrinsic electrical conductivity and whether it can be intrinsically improved by multivalent-ion doping at the Li or Fe sites. Significant enhancement of conductivity has been observed in polycrystalline LFPO doped with Mg, Ni, Co, Nb, Zr, and Ti.^{3,4} However, the underlying mechanisms for the enhancement are still very controversial and not fully understood, as some conductive impurities were found in the doped LFPO polycrystalline powders and bulks.⁵ On the other hand, the LFPO compound also exhibits interesting electric structures and magnetic properties, such as spin polarization⁶ and one-dimensional antiferromagnetism along the (010) direction.⁷ So far, polycrystalline powders and bulk samples have been commonly used in investigations of LFPO.^{6–9} However, sizable and high quality crystals are much more desirable for the study of the intrinsic structural, physical, and chemical properties, and particularly for the electronic and magnetic anisotropies. In this work, we report on our investigations of the magnetic anisotropy in LiFePO_4

and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ single crystals grown by a floating zone method. The results on the crystal structures and magnetic anisotropy properties are presented.

II. EXPERIMENT

LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ powders were synthesized by solid-state reactions using Li_2CO_3 (99.999%), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.999%), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.999%), and $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (99.999%) as the precursor reagents. The single crystals were grown using the traveling solvent floating zone (TSFZ) method with a stoichiometric self-flux.¹⁰ Single crystal samples were oriented using standard Laue diffraction and cut into cubes along the a , b , and c directions. X-ray diffraction (XRD) analysis using $\text{Cu K}\alpha$ radiation was performed to identify the phase purity and sample orientations. Elemental compositions of samples were determined by inductively coupled plasma (ICP). The magnetic susceptibility measurements were carried out using a superconducting quantum interference device magnetometer (Quantum Design, model MPMS 7.0) over a wide range of temperatures from 10 to 340 K under a magnetic field of 1 T.

III. RESULTS AND DISCUSSION

Slices of as-grown crystal ingots were cut into cubic bulks whose surfaces were polished to mirrorlike faces. All the samples are blackish green in color, and the Mg doped sample was found to be darker than the undoped LFPO. The Li, Fe, P, and Mg contents were found to be equal to the starting compositions. Single crystal XRD measurements were also made on the cubic specimens. The typical XRD patterns obtained from three orientations are shown in Fig. 1 for both pure and Mg doped crystals. All the peaks of each pattern can be indexed by the $(h00)$, $(0k0)$, and $(00l)$ diffraction

^{a)}Author to whom correspondence should be addressed; electronic mail: xiaolin@uow.edu.au

FIG. 1. X-ray diffraction patterns for LiFePO_4 (a) and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ (b) single crystals cut along the a , b , and c directions (from top to bottom). All the peaks can be attributed to $(h00)$, $(0k0)$, and $(00l)$, respectively.

tion peaks of LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$, respectively. The lattice parameters were estimated to be $a=10.33$ Å, $b=6.01$ Å, and $c=4.69$ Å for LiFePO_4 and $a=10.25$ Å, $b=6.01$ Å, and $c=4.70$ Å for $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$. These values are in agreement with the reported crystal data^{7,11} determined from polycrystalline samples. No traces of impurities or inclusions were observed in our crystal samples.

Figure 2 shows the variation of zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities with tempera-

FIG. 2. Magnetic susceptibility of single crystal LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ measured in $H=1$ T magnetic field applied along the three principal axes.

FIG. 3. Temperature dependence of the susceptibility for two single crystals. The solid lines are fits to the data.

ture in the range of 10–340 K for both LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ cubic single crystals. Both FC and ZFC susceptibilities were measured under an applied field of 1 T along the a , b , and c directions. All the curves show that both samples are characterized by typical paramagnetic features over a wide temperature range and become antiferromagnetic at a Néel temperature of 53 K for LiFePO_4 and 52 K for $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$. An up-turn in the susceptibility starts from about 32 K along the a and c directions for both samples, and the upturn is steep for the Mg doped crystals due to the Mg doping effect.

Signs of a long-range Néel ordering are also clearly seen. Below 52 K a substantial drop is observed in χ_b , while both χ_a and χ_c change little from 52 K down to 10 K. This clearly indicates the presence of antiferromagnetic long-range order below T_N with the crystallographic b axis being the magnetic easy axis of the system for both compositions. Note that at $T \rightarrow 0$, χ_b retains a substantial nonzero value, suggesting a reduction of ordered moment, presumably due to the one dimensional nature of the system, as seen in Ref. 12. This agrees with the fact that the magnetic moments of the iron atoms in the unit cell are oriented along $[010]$ for LiFePO_4 .⁷

We fit the temperature dependence of the susceptibility of both single crystals to a modified Curie-Weiss law, as shown in Fig. 3, $\chi = \chi_0 + C/(T - \theta)$, where χ_0 , C , and θ are the temperature independent susceptibility, the Curie constant, and the Curie-Weiss temperature, respectively. The solid lines represent the fit to the experimental data in the temperature range of 70–340 K.

The results of the fitting are given in Table I. The fitted values for the powder average values are also listed. As expected, we find that the Curie constants for $H\parallel b$ are significantly different from those for $H\parallel a$ and $H\parallel c$, while the Mg doped crystal shows a larger difference between $H\parallel a$ and $H\parallel c$ than the undoped one.

The value of the constant susceptibility term χ_0 is of the order of 10^{-3} emu/mole Oe for both pure and Mg doped LFPO. The negative θ values suggest antiferromagnetically interacting spins, and $|\theta|$ increases in the order of $H\parallel b$, $H\parallel a$,

TABLE I. Summary of magnetic data for LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$.

Sample	Field orientation	C ($\text{cm}^3 \text{ K/mole}$)	θ (K)	χ_0 ($\text{emu/mole}_{\text{Fe}^{2+}}$)
LiFePO_4	$\parallel a$	4.67(2)	-119.9(5)	0.001 87(3)
	$\parallel b$	5.31(3)	-105.6(9)	0.001 36(6)
	$\parallel c$	4.60(2)	-160.7(1)	0.001 54(3)
	Average	4.77(2)	-123.0(6)	0.001 69(4)
$\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$	$\parallel a$	4.86 (2)	-118.7(5)	0.000 90 (3)
	$\parallel b$	5.39(4)	-102.0(9)	0.001 31(7)
	$\parallel c$	4.14(2)	-137.5(7)	0.001 26(3)
	Average	4.61(1)	-110.4(4)	0.001 43(3)

and $H \parallel c$. The powder averaged Curie constant gives an effective magnetic moment of $\mu_{\text{exp}} = 6.18\mu_B$ for LiFePO_4 and $\mu_{\text{exp}} = 6.07\mu_B$ for $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$, where μ_B is the Bohr magneton. Our experimental data are between the published values obtained from polycrystalline bulks or powders.^{6,8,13}

However, these values are higher than what is expected on the basis of the spin only value ($4.90\mu_B$). This implies that orbital contributions might need to be taken into account. The Fe^{2+} ion presents a high spin d^6 configuration in a weak crystal field with four electrons (spin up) on each e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}). This configuration corresponds to $S=2$, $L=2$, and consequently $J=4$. If there is no orbital moment quenching, the effective Bohr magnetron number defined as the formula $P_{\text{eff}} = g[J(J+1)]^{1/2}$, and the value of the g factor calculated by Landé's equation is $g=3/2$. The estimated effective magnetic moment is about $6.70\mu_B$, which is relatively close to what we have obtained from our single crystal samples.

IV. CONCLUSION

Single crystals of LiFePO_4 and $\text{Li}_{0.99}\text{Mg}_{0.01}\text{FePO}_4$ grown using the optical floating zone technique reveal a con-

siderable anisotropy in the susceptibilities along $H \parallel a$, $H \parallel b$, and $H \parallel c$. Both pure and Mg doped crystals show antiferromagnetic behavior below 52 K along the b , a , and c directions with the crystallographic b axis being the magnetic easy axis for both crystals. The effective moments have been determined to be $6.18\mu_B$ and $6.07\mu_B$ for pure and doped crystals, respectively. These values are higher than what is expected on the basis of the spin-only value ($4.90\mu_B$) and close to what is estimated considering both the spin and orbital coupling with a high-spin d^6 configuration for the Fe^{2+} ion.

ACKNOWLEDGMENTS

This work is supported in part by funding from the Australian Research Council through Discovery project (DP0558753).

- ¹A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.* **144**, 1188 (1997).
- ²C. M. Julien, K. Zaghib, A. Mauger, M. Massot, A. Ait-Salah, M. Selmane, and F. Gendron, *J. Appl. Phys.* **100**, 063511 (2006).
- ³D. Wang, H. Li, S. Shi, X. Huang, and L. Chen, *Electrochim. Acta* **50**, 2955 (2005).
- ⁴N. Ravet, A. Abouimrane, and M. Armand, *Nat. Mater.* **2**, 702 (2003).
- ⁵S.-Y. Chung, J. T. Bloking, and Y.-M. Chiang, *Nat. Mater.* **1**, 123 (2002).
- ⁶P. Tang and N. A. W. Holzwarth, *Phys. Rev. B* **68**, 165107 (2003).
- ⁷G. Rousse, J. Rodriguez-Carvajal, S. Patoux, and C. Masquelier, *Chem. Mater.* **15**, 4082 (2003).
- ⁸R. P. Santoro and R. E. Newnham, *Acta Crystallogr.* **22**, 344 (1967).
- ⁹A. Ait-Salah, J. Dodd, A. Mauger, R. Yazami, F. Gendron, and C. M. Julien, *Z. Anorg. Allg. Chem.* **632**, 1598 (2006).
- ¹⁰D. P. Chen, A. Maljuk, and C. T. Lin, *J. Cryst. Growth* **284**, 86 (2005).
- ¹¹O. Garcia-Moreno, M. Alvarez-Vega, F. Garcia-Alvarado, J. Garcia-Jaca, J. M. Gallardo-Mores, M. L. Sanjuan, and U. Amador, *Chem. Mater.* **13**, 1570 (2001).
- ¹²I. Tsukada, Y. Sasago, K. Uchinokura, A. Zheludev, S. Maslov, G. Shirane, K. Kakurai, and E. Ressouche, *Phys. Rev. B* **60**, 6601 (1999).
- ¹³M. C. Tücher, M. M. Döeff, T. J. Richardson, R. Finones, E. J. Cairns, and J. A. Reimer, *J. Am. Chem. Soc.* **124**, 3832 (2002).