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](https://ro.uow.edu.au/engpapers)  
Part of the Engineering Commons  

**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.  

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Magnetic anisotropy in doped and undoped LiFePO₄ single crystals

D. P. Chen and Xiaolin Wang
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

(Received 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 LiFePO₄ single crystals grown by the traveling solvent floating zone technique. Our results reveal a considerable anisotropy in the susceptibilities along H||a, H||b, and H||c for both crystals. LiFePO₄ and Li₀.⁹⁹Mg₀.⁰¹FePO₄ 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 6.18μ₉ and 6.07μ₉ 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 6.70μ₉ with a high-spin d⁶ configuration for the Fe²⁺ ion. © 2007 American Institute of Physics. [DOI: 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, LiFePO₄ (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. 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. 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. On the other hand, the LFPO compound also exhibits interesting electric structures and magnetic properties, such as spin polarization and one-dimensional antiferromagnetism along the (010) direction. So far, polycrystalline powders and bulk samples have been commonly used in investigations of LFPO. 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 LiFePO₄ and Li₀.⁹⁹Mg₀.⁰¹FePO₄ single crystals grown by a floating zone method. The results on the crystal structures and magnetic anisotropy properties are presented.

II. EXPERIMENT

LiFePO₄ and Li₀.⁹⁹Mg₀.⁰¹FePO₄ powders were synthesized by solid-state reactions using Li₂CO₃ (99.999%), FeC₂O₄·2H₂O (99.999%), NH₄H₂PO₄ (99.999%), and MgC₂O₄·2H₂O (99.999%) as the precursor reagents. The single crystals were grown using the traveling solvent floating zone (TSFZ) method with a stoichiometric self-flux. 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 Cu Kα 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 peaks.
tion peaks of LiFePO\(_4\) and Li\(_{0.99}\)Mg\(_{0.01}\)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 Li\(_{0.99}\)Mg\(_{0.01}\)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 temperature in the range of 10–340 K for both LiFePO\(_4\) and Li\(_{0.99}\)Mg\(_{0.01}\)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 Li\(_{0.99}\)Mg\(_{0.01}\)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 steeper 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 \(\chi_b\), while both \(\chi_a\) and \(\chi_c\) 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 \(T \rightarrow 0\), \(\chi_b\) 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 \(\chi_0\), \(C\), and \(\theta\) 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 \(H || b\) are significantly different from those for \(H || a\) and \(H || c\), while the Mg doped crystal shows a larger difference between \(H || a\) and \(H || c\) than the undoped one.

The value of the constant susceptibility term \(\chi_0\) is of the order of \(10^{-3}\) emu/mole Oe for both pure and Mg doped LFPO. The negative \(\theta\) values suggest antiferromagnetically interacting spins, and \(|\theta|\) increases in the order of \(H || b\), \(H || a\), and \(H || c\).
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 Li$_{0.99}$Mg$_{0.01}$FePO$_4$, where $\mu_B$ is the Bohr magneton. Our experimental data are between the published values obtained from polycrystalline bulks or powders. 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 ($d_{x^2}$-$d_{y^2}$ 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 magneton number defined as the formula $P_{\text{eff}} = g(J+1)$, 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 Li$_{0.99}$Mg$_{0.01}$FePO$_4$ grown using the optical floating zone technique reveal a considerable 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).