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Mössbauer study and magnetic properties of electrochemical material $LiFePO_4$*

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Magnetic properties and crystal symmetry of electrochemical material $LiFePO_4$ have been investigated by Mössbauer spectroscopy and magnetization measurement. Magnetization reveals the antiferromagnetic nature of $LiFePO_4$. Temperature dependence of inverse susceptibility and that of hyperfine field confirm that there is an antiferromagnetic-paramagnetic transition at about 50K.

Keywords: lithium-polymer battery, Mössbauer spectroscopy, lithium iron phosphates
PACC: 7680, 7550E, 7530C

1. Introduction

$LiFePO_4$ has received much attention as a promising cathode material for its high energy density, very good cycling capability and stability at low current density.[1,2] As the energy of a given redox couple depends on the electrostatic field at the cation position and the covalent contribution to the cation–anion bonding, and the structural change will lead to a change in electrostatic field, it is important to understand the structure features of the material. Recently, a change from electrochemically active to electrochemically inactive due to a structural phase transition was reported.[3] However, very little is known about its low-temperature properties, especially the magnetic property. Santoro and co-workers have reported that Fe–O–Fe superexchange coupling gives rise to antiferromagnetic puckered-planes orthogonal to the a-axis. $LiFePO_4$ is antiferromagnetic below the Néel temperature (∼50K). There may be Fe–O–P–O–Fe triple exchange between these planes.[4] The multipole charge-density model refinement of x-ray diffraction (XRD) data confirms this picture.[5] The Mössbauer spectrum is very sensitive to the magnetic moment and the crystal field at the iron site. It can provide information about the magnetic property and microscopic structure. By considering the central shift, the valence of Fe ions can also be determined. In this paper we discuss the Mössbauer and magnetic studies of $LiFePO_4$, focusing on the magnetic property and the crystal symmetry.

2. Experiment

XRD data were collected by a Rikagu diffractometer. Magnetization was measured with a SQUID magnetometer under an external magnetic field of 1T. Transmission Mössbauer spectra were collected using a $^{57}Co(Rh)$ source in a constant acceleration mode. Zero-field Mössbauer spectra have been recorded at various temperatures using a closed cycle refrigerator. The central shift values are obtained relative to α-Fe at room temperature.

3. Results and discussion

The refinement result of XRD pattern is shown in Fig.1. $LiFePO_4$ has an olivine-type struc-

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ture, the space group is *Pnma*, a=1.031982(23)nm, b=0.600275(14)nm, c=0.469066(11)nm. FeO_6 octahedra are linked through common corners in the bc-plane, and LiO_6 octahedra form edge-sharing chains along the b-axis. One FeO_6 octahedron has common edges with two LiO_6 octahedra and a PO_4 tetrahedron. PO_4 tetrahedron has three of the six edges in common with the cation octahedral.[1,5] The XRD result indicates that the Fe cation lies in a distorted octahedron (Fig.2). Here the poor fitting result of low-angle diffraction may be caused by the existence of impurities.

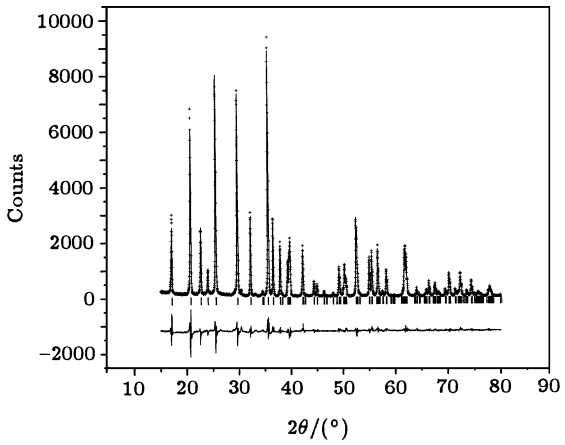


Fig.1. The Rietveld refinement of XRD data. Starting atomic coordinates of $LiFePO_4$ were taken from Streltsov *et al*[5] During the process of refinement only one phase, $LiFePO_4$, is included. R_p:8.49%, R_{wp}:12.01%, R_{exp}:5.35%.

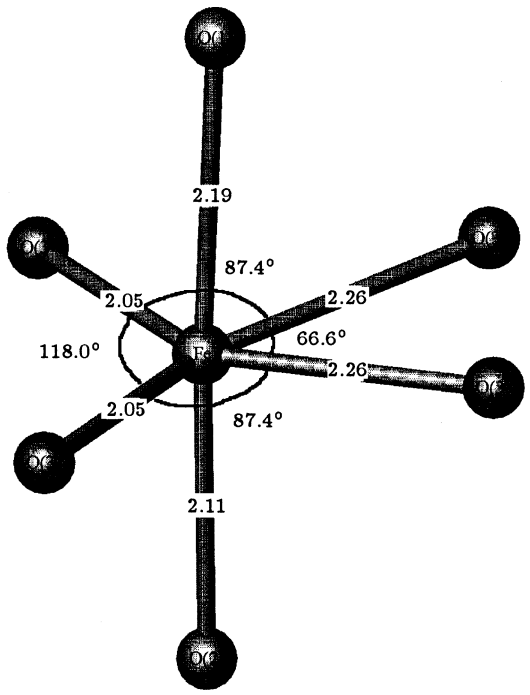


Fig.2. Sketch of the local structure of Fe atom. Other atoms are omitted for clarity.

Temperature dependence of the inverse susceptibility at 1T external magnetic field is shown in Fig.3. The inverse susceptibility shows a minimum at 49±2K, indicating a magnetic phase transition at that point. In the paramagnetic region, it follows a typical Curie–Weiss behaviour, $1/\chi = \left(\frac{T-\theta}{C}\right)$. By fitting all data in this region, a negative θ is determined. The magnetization at 5K varies nearly linearly with the external magnetic field and does not saturate even up to 5T (Fig.4). This confirms the antiferromagnetic order at low temperatures.

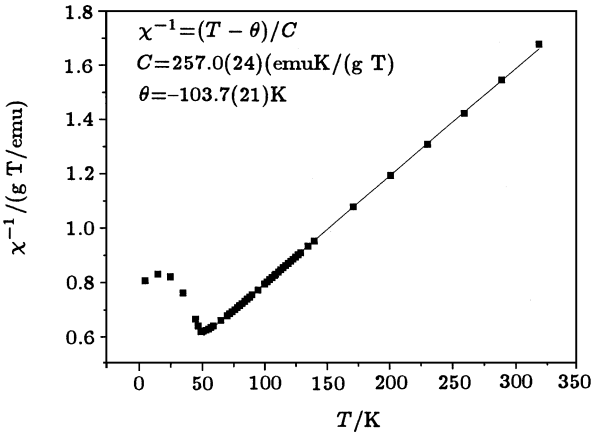


Fig.3. Temperature dependence of the inverse susceptibility.

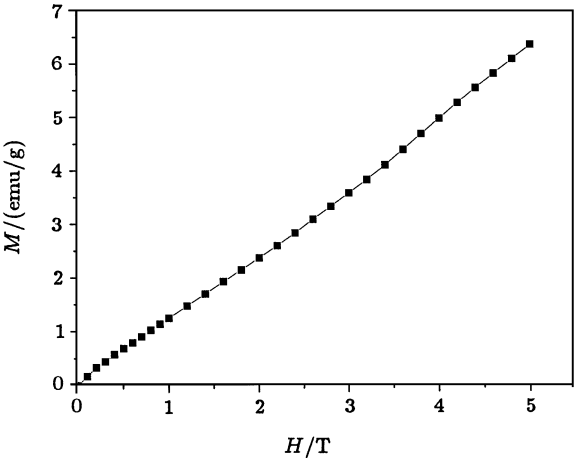


Fig.4. Isothermal magnetization curve at 5K.

Mössbauer spectroscopy has been a tool to study the evolution of $LiFePO_4$ in the charge–discharge procedure, and it is very sensitive to the impurity phases.[1,6] In this work we carry out Mössbauer study as a way to investigate the magnetic properties. Mössbauer spectra of $LiFePO_4$ at 5, 50K and room

temperature are shown in Fig.5. All spectra below 50K can be fitted with one doublet and a sextet, while the spectra above 60K can be fitted with two doublets. For the spectrum of 50K one sextet and two doublets are needed to best fit the spectrum. All these spectra originate from high spin Fe^{2+}, as was confirmed by the typical central shift (δ) value (+0.8 to +1.5mm/s) for high spin Fe^{2+}.[7] However, the proportion of the two components of doublet at low temperatures does not change as temperature rises, so it must come from a second phase. For if it comes from fine particles, the proportion should change. But, unfortunately, in the paramagnetic region, for the poor resolution, it is difficult to separate the two components. So we fixed the hyperfine parameters of the impurity phase as it is at low temperatures and with its proportion about 8%. The coexistence of the paramagnetic and antiferromagnetic components of $LiFePO_4$ at 50K indicates that there is an antiferromagnetic–paramagnetic transition at about 50K. Hyperfine parameters at different temperatures are listed in Table 1. The result of $LiFePO_4$ at room temperature is consistent with that of previous works.[1,6]

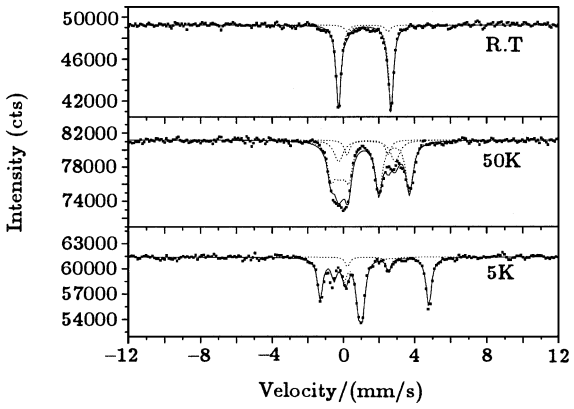


Fig.5. Mössbauer spectra of $LiFePO_4$ in zero-field.

Table 1. Hyperfine parameters of $LiFePO_4$ at selected temperatures (δ: central shift relative to metallic α-Fe at room temperature; Δ: quadrupole shift; H_{hf}: hyperfine field; Γ: full-width at half-maximum of the peaks; A: proportion of different subspectra.)

T/K	δ/(mm/s)	Δ/(mm/s)	$H_{hf}/(10^5 A/m)$	$\Gamma/2$/(mm/s)	A/%
5	1.35(1)	1.58(1)	91.88(40)	0.14(5)	91.9(34)
	1.39(0)	2.31(7)	–	0.14(5)	8.1(23)
20	1.34(1)	1.56(1)	91.53(27)	0.19(1)	92.8(21)
	1.37(2)	2.30(0)	–	0.13(3)	7.2(14)
30	1.34(1)	1.56(1)	89.72(28)	0.18(8)	93.5(24)
	1.37(2)	2.30(4)	–	0.11(4)	6.5(15)
40	1.35(1)	1.55(1)	77.55(40)	0.20(1)	92.0(34)
	1.41(5)	2.42(1)	–	0.19(8)	8.0(24)
50	1.33(3)	3.16(6)	–	0.30(1)	19.5(50)
	1.34	2.3	–	0.18	8.1
	1.34(1)	1.52(2)	42.50(58)	0.24(2)	72.4(51)
60	1.36(2)	3.04(1)	–	0.20(1)	92.0
	1.34	2.3	–	0.18	8.0
70	1.36(2)	3.10(1)	–	0.20(1)	92.2
	1.34	2.3	–	0.18	7.8
RT	1.22(1)	2.94(1)	–	0.159(7)	92.2
	1.34	2.3	–	0.18	7.8

On the basis of the temperature dependence of the magnetic hyperfine field, the transition point of antiferromagnetic phase can be also determined. In order to determine the Néel temperature, T_N, we have measured Mössbauer spectra at various temperatures. Temperature dependence of the hyperfine field is shown in Fig.6. As the temperature approaches 50K, the H_{hf} decreases rapidly and at 60K the value of H_{hf} is zero; some of $LiFePO_4$ has changed into paramagnetic phase even at 50K. So we can conclude that the transition point is about 50K.

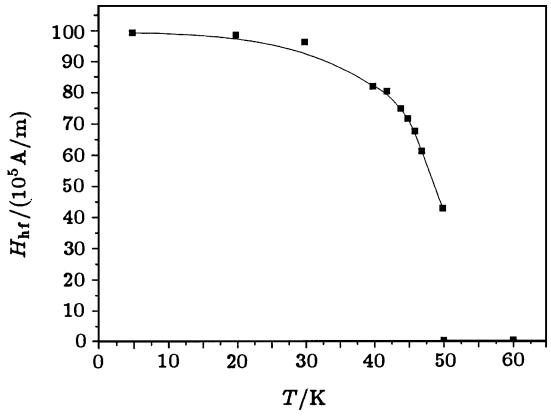


Fig.6. Temperature dependence of H_{hf}. The line is a guide for the eyes.

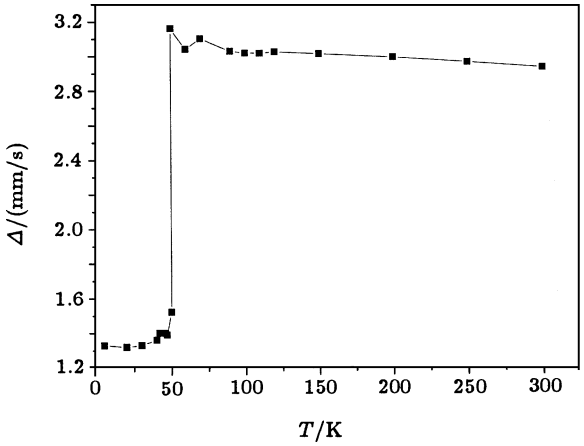


Fig.7. Temperature dependence of Δ of $LiFePO_4$. The line is guide for eyes.

XRD shows that the Fe atom lies in a distorted octahedron. And the multipole charge-density model refinement of XRD data reveals that the electron density distribution of the 3d electrons is asymmetric. The occupancies of the five 3d-orbitals of the Fe atom are different.[5] They lead to large V_{zz}, which results in the large quadrupole shift Δ.

The temperature dependence of Δ is shown in Fig.7. The change of Δ is caused by the influence of hyperfine field. Under the first-order perturbation, the quadrupole shift can be expressed as

$$\Delta(T < T_N) = \frac{eQV_{zz}}{2}(3\cos^2\theta - 1),$$

where θ is the angle between the hyperfine field and the principal component of the electric field gradient. Here we can see that when antiferromagnetic–paramagnetic transition occurs, the term associated with θ disappears, and Δ may change at the transition point. So the transition point is about 50K for $LiFePO_4$, judging from the jump of Δ at that point.

4. Conclusion

Magnetization and Mössbauer study of $LiFePO_4$ show that an antiferromagnetic–paramagnetic transition occurs at Néel temperature(~50K). The asymmetric local structure and the distribution of 3d electrons lead to a large quadrupole shift.

Acknowledgement

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References

[1] Andersson A S *et al* 2000 *Solid State Ionics* **130** 41
[2] Yang S *et al* 2002 *Electrochem. Commun.* **4** 239
[3] García-Moreno O *et al* 2001 *Chem. Mater.* **13** 1570
[4] Santoro R P *et al* 1967 *Acta Crystallogr.* **22** 344
[5] Streltsov V A *et al* 1993 *Acta Crystallogr.* B **49** 147
[6] Yamada A *et al* 2001 *J. Electrochem. Soc.* **148** A960
[7] Chmaissem O *et al* 2000 *Phys. Rev.* B **62** 14197