



Article

ESR Investigations of the Submicron $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ Systems

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Abstract: Magnetic properties of the submicron carbon-coated $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$) systems were investigated using the electron spin resonance (ESR) method. The observed ESR signal consisted of two broad resonance lines with a Lorentzian line shape for all samples. The temperature dependence character of the integral intensity of these lines changed significantly with increasing manganese concentration, indicating a change in the nature of the magnetic interactions between the manganese and iron ions. We suggest that the noticeable capacity loss observed in the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ systems with increasing Mn content can be explained by the random distribution of Mn ions and changes to the type of magnetic ordering in these systems, despite the attractiveness of the electrochemical $\text{Mn}^{2+}/\text{Mn}^{3+}$ pair compared with $\text{Fe}^{+2}/\text{Fe}^{+3}$.

Keywords: $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$; cathode material; electron spin resonance



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1. Introduction

Phospho-olivines were proposed as positive-electrode materials for rechargeable lithium batteries several decades ago [1], and today, they are already widely used in commercial lithium-ion batteries for mobile devices, energy storage power stations, and other applications. Among the different phospho-olivines, the lithium-iron phospho-olivine enables the utilization of 95% of the theoretical capacity (170 mAh/g) at room temperature [2,3] and has environmental and cost advantages. However, the significant limitation for the further commercial application of these phospho-olivines is their rapid capacity degradation at extreme low and high temperatures. Some accelerated fading mechanisms of LiFePO_4/C batteries at room temperature and under extreme temperatures, and the progress made in the modification strategies, are discussed in [4,5]. The increased ohmic resistance due to the growth of the solid electrolyte interface, the reduced reaction kinetics of Li^+ due to the complication of the energy pathway between the $\text{LiFePO}_4/\text{FePO}_4$ phases during the lithium extraction/insertion process at low temperatures, and the limited ionic diffusion rate in the electrolyte can cause the degradation of LiFePO_4/C batteries at low temperatures [5]. The physical properties of lithium-iron phospho-olivines have also been intensively theoretically studied. Recent achievements in first-principles studies of LiFePO_4 cathode materials are discussed in [6], including findings on the structure, electronic properties, Li-ion transport characteristics, mechanical stability, and thermodynamic properties that can provide a better understanding of the modification direction for olivine-type materials. Among others, the ion substitution method (on either Li or Fe sites) can be considered as one of the directions for modification [7]. While the most favorable intrinsic

defect in LiFePO_4 is the Li-Fe “anti-site” pair, in which a Li ion and an Fe ion are interchanged, LiFePO_4 is not tolerant to aliovalent doping on energetic grounds, and favorable low energies are found only for divalent dopants on the Fe site (such as Mn) [8].

A general overview of the structural features, typical electrochemical behavior, delithiation/lithiation mechanisms, and thermodynamic properties of $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$ ($0.5 \leq y < 1.0$), as well as recent developments in the improvement of the electrochemical performance of $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$ -based materials, are summarized in [9], including the selection of the synthetic methods, nanostructuring, surface coating, optimizing Fe/Mn ratios and particle morphologies, and others. In addition to the above-mentioned work, the impact of carbon coating on the specific surface area and the discharge profiles of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ were investigated in [10]; the influence of different Fe/Mn ratios on the morphology and the electrical and electrochemical performances of $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4/\text{C}$ nanofiber composites were analyzed in [11]; the effects of the intensity of high-energy ball-milling on the porous structure and electrochemistry of LFMP/C were studied in [12]; and the influences of the synthesis method and morphology on the electrochemical properties have been observed by comparing (i) mechanochemical and solvothermal methods [13], (ii) the sol-gel route combined with freeze drying [14] and high-energy ball-milling-assisted sol-gel methods [15], (iii) the rheological phase method [16], and others.

It is known from the literature that, in some synthesis methods (e.g., the solvothermal method), $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples have two different phases: LiFePO_4 and LiMnPO_4 , which are randomly stacked and characterized by a pronounced structural distortion of the MO_6 ($\text{M} = \text{Fe}$ or Mn) octahedral, with the best electrochemical performance exhibited by the $\text{LiFe}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ sample [17]. The thermodynamic behavior of Mn-doped LiFePO_4 cathodes was also recently examined through first-principles simulations using the multi-phase object $\text{Li}(\text{Mn}_y\text{Fe}_{1-y})\text{PO}_4$ - $(\text{Mn}_y\text{Fe}_{1-y})\text{PO}_4$ [18]. The investigation of $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4/\text{C}$ ($y = 0$ – 0.3) nanocomposites demonstrated that samples with a low manganese content are characterized by increased conductivity and enhanced charge/discharge capacity, especially at high current density, and the regions with an inhomogeneous distribution of divalent and trivalent manganese ions are formed in $\text{Li}_x\text{Fe}_{0.7}\text{Mn}_{0.3}\text{PO}_4$ [19].

Here, we present a detailed investigation of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ using the electron spin resonance method. It is well known that the electron spin resonance (ESR) method is a highly sensitive experimental technique that allows us to detect resonance signals from objects which cannot be registered either by X-ray structural analysis or by electron microscopy, and that offers us the possibility of studying magnetic phase separation. The detailed XRD, Mössbauer, and NMR spectroscopy, and the magnetic susceptibility measurements of carbon-coated $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($0 \leq x \leq 1$) samples, which were synthesized by the same method as the one studied in this work, are presented in [20]. In this work, we focus on submicron carbon-coated $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples with low manganese concentrations ($x = 0.01, 0.1$), in addition to the initial LiFePO_4 .

2. Experimental Results

The $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples were prepared by the mechanochemically assisted carbothermal reduction of Li_2CO_3 , Fe_2O_3 , MnO_2 , and $(\text{NH}_4)_2\text{HPO}_4$ using the high-energy planetary mill, as described in [20,21]. Electron spin resonance (ESR) measurements were carried out using the continuous wave (CW) EPR spectrometer BER-218S (Bruker, Germany) at the frequency of 9.58 GHz (X-band) in the temperature range from 7 K to 300 K. The modulation of the applied magnetic field was used to detect the first derivative of the absorption power dP/dH in order to increase the signal-to-noise ratio of the experiment. The modulation frequency was 100 kHz and the modulation amplitude was 10 Oe.

The ESR spectra of the initial LiFePO_4 and manganese-substituted $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0.01, 0.1$) samples measured at different temperatures are presented in Figure 1. The intensity of some experimental spectra was multiplied for clarity: at low temperatures for the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0$ and 0.01) samples, and at high temperatures for the $\text{LiFe}_{0.9}\text{Mn}_{0.1}\text{PO}_4$ samples, respectively, indicating the different behavior of the integral intensity of the ESR

spectra with a change in temperature. Figure 2 shows the concentration evolution of the ESR spectra at a fixed temperature. One can see that the ESR spectra have a similar line shape for all samples at room temperature, and they are very different at $T = 50$ K.

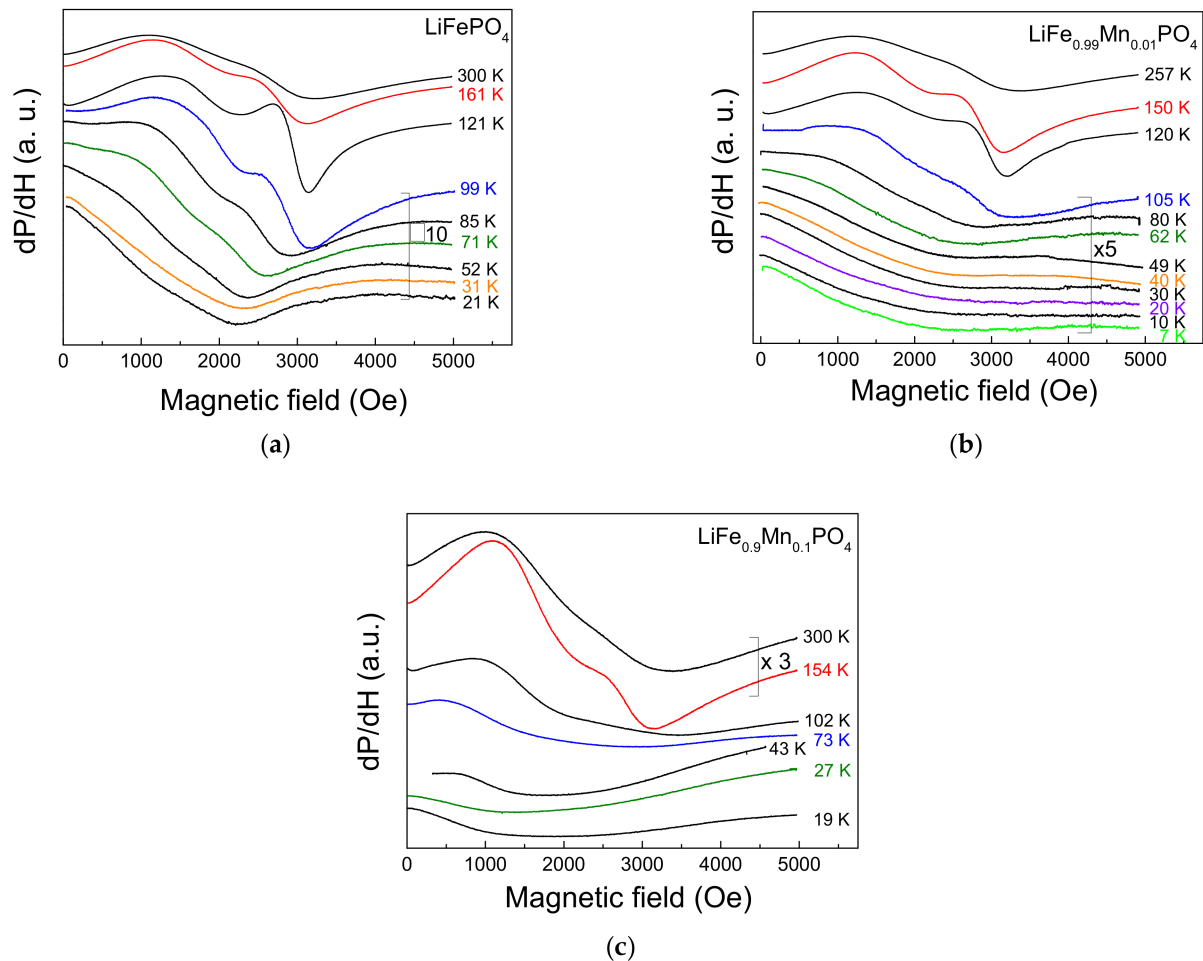


Figure 1. Electron spin resonance spectra of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$: (a) $x = 0$, (b) $x = 0.01$, and (c) $x = 0.1$ at different temperatures. The intensity of some experimental spectra was multiplied for clarity.

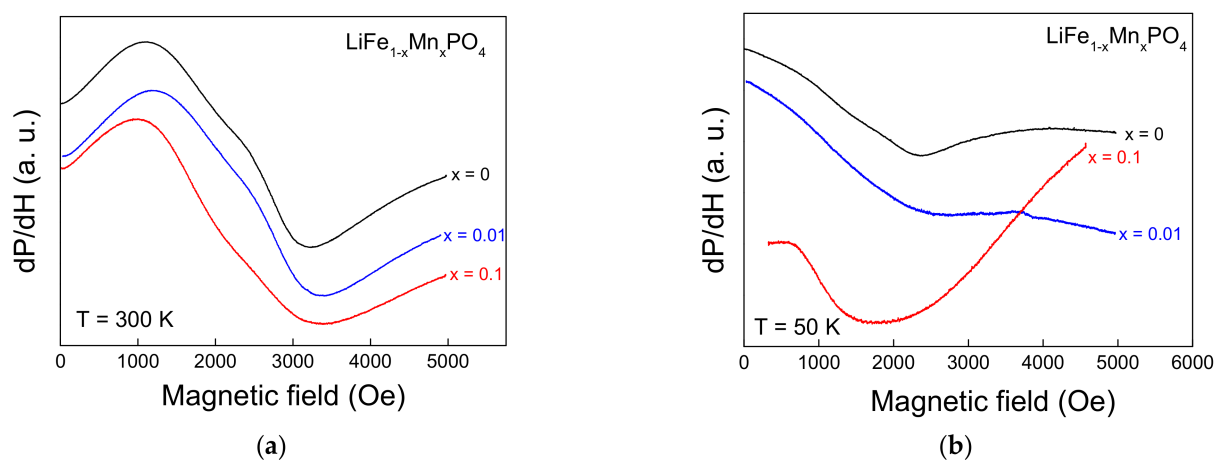


Figure 2. ESR spectra of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ at the temperatures of (a) 300 K and (b) 50 K.

In all temperature ranges, the ESR spectra of the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ samples can be described by the sum of two exchange-narrowed resonance lines, which is well fitted by

the asymmetric Lorentzian line shape that includes the circular components of the exciting linearly polarized microwave with the resonance at the reversed magnetic field $-H_0$ [22]:

$$\frac{dP}{dH} = \frac{d}{dH} \left(\frac{\Delta H + \alpha(H - H_0)}{\Delta H^2 + (H - H_0)^2} + \frac{\Delta H - \alpha(H + H_0)}{\Delta H^2 + (H + H_0)^2} \right) \quad (1)$$

Equation (1) includes both absorption and dispersion, where α denotes the dispersion-to-absorption (D/A) ratio. It should be noted that α was taken equal to zero to describe the experimental data. Equation (1) should be used when the linewidth ΔH is on the same order of magnitude as the resonance field H_0 [23,24], which was also observed in the investigated samples. The fitted ESR spectrum was calculated as the sum of Equation (1) multiplied by the amplitude (A) of line 1 and line 2, respectively.

The decomposition details of the magnetic resonance spectra are given in Figures 3–5 for $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ with $x = 0, 0.01$ and 0.1 , respectively. Temperature dependencies of the ESR spectra parameters (g-factors, linewidth ΔH , and normalized integral intensity I) are shown in Figures 6–8, respectively; g-factors were obtained as $g = h\nu / \mu_B \cdot H_{\text{res}}$ (ν —X-band frequency, μ_B —Bohr magneton, H_0 —resonance field). The normalized integral intensity was obtained as the integral intensity $I = A \cdot \Delta H^2$ (A—signal amplitude, ΔH —ESR linewidth) divided by the maximum value of the two lines I_{max} in order to compare the integrated intensities of the two components of the ESR spectrum with one another. It should be noted that, due to the large values of the ESR linewidth, the spectra parameters can be determined with an error: each ESR spectrum was fitted by several algorithms and using several sets of initial ESR parameters. As a result, several sets (3–5) of ESR parameters were obtained for the same spectrum, which correlated with one another qualitatively and had some quantitative dispersion. The average values of the ESR parameters are shown in Figures 6–8 together with an error that was obtained as the standard deviation from the mean.

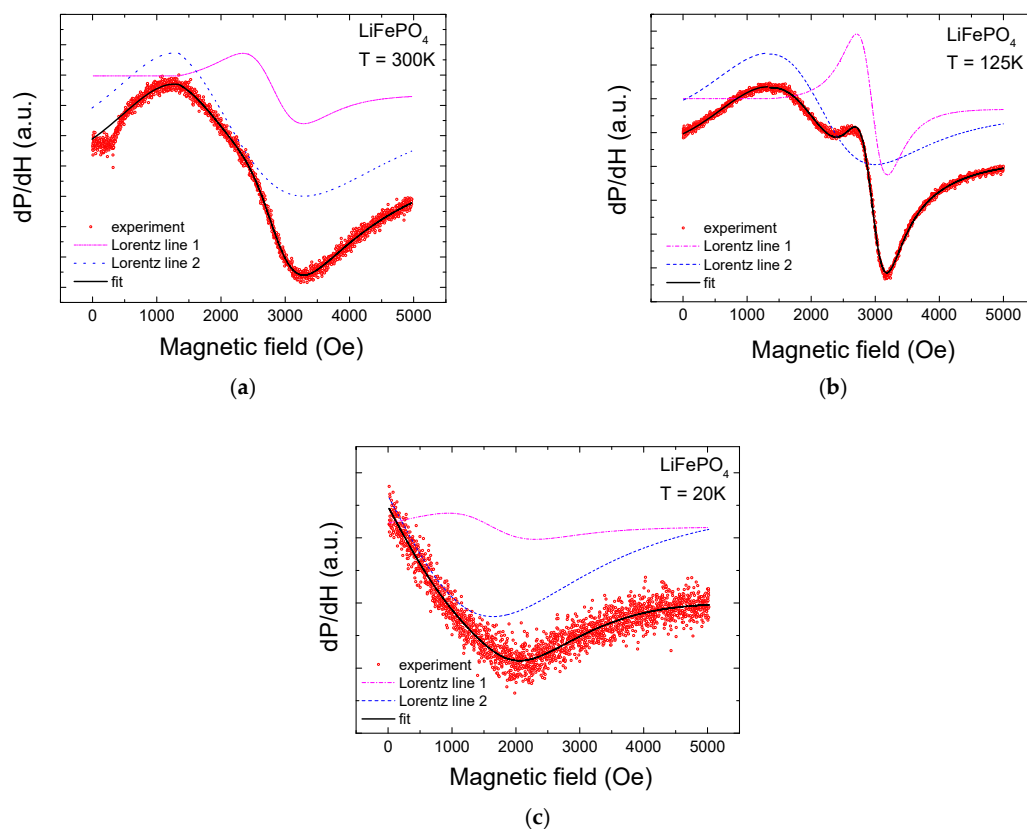


Figure 3. Decomposition of the ESR spectra of LiFePO_4 at different temperatures: (a) $T = 300$ K, (b) $T = 125$ K, and (c) $T = 20$ K.

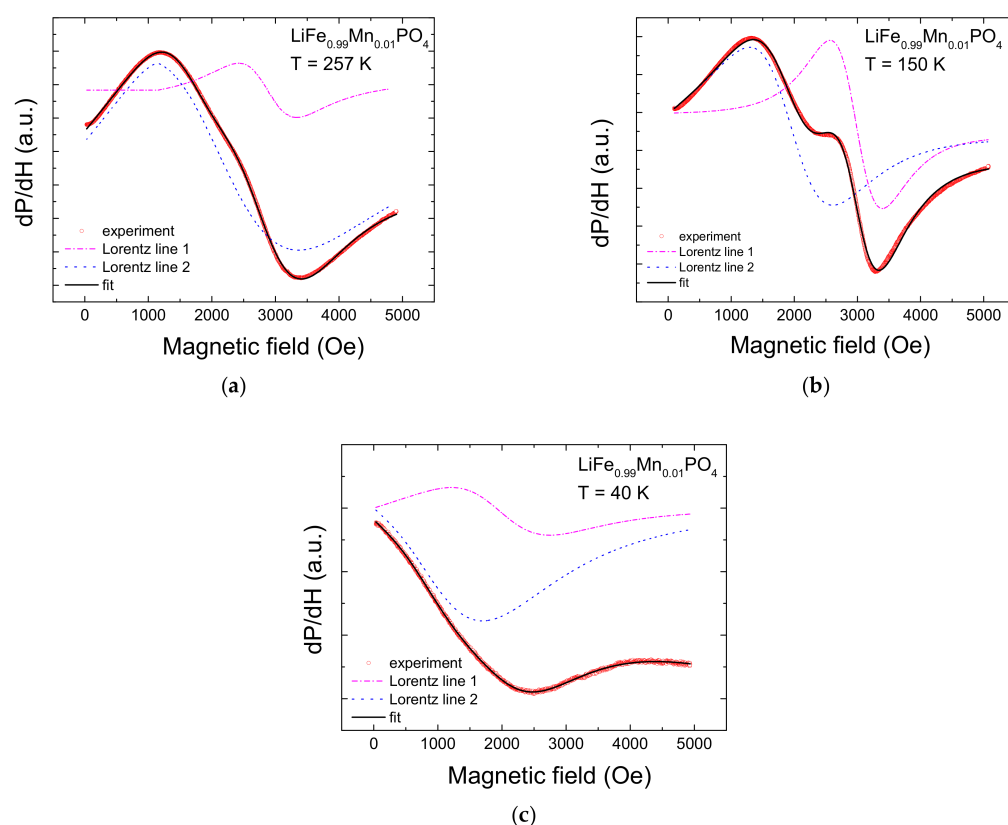


Figure 4. Decomposition of the ESR spectra of $\text{LiFe}_{0.99}\text{Mn}_{0.01}\text{PO}_4$ at different temperatures: (a) $T = 257 \text{ K}$, (b) $T = 150 \text{ K}$, and (c) $T = 40 \text{ K}$.

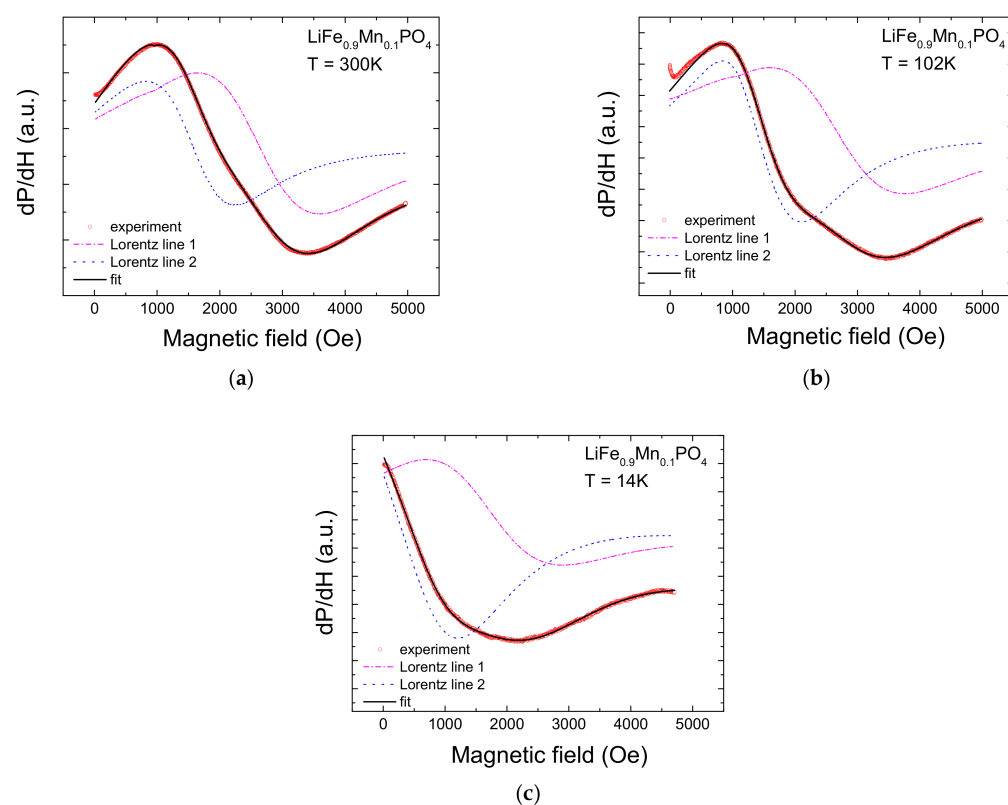


Figure 5. Decomposition of the ESR spectra of $\text{LiFe}_{0.9}\text{Mn}_{0.1}\text{PO}_4$ at different temperatures: (a) $T = 300 \text{ K}$, (b) $T = 102 \text{ K}$, and (c) $T = 14 \text{ K}$.

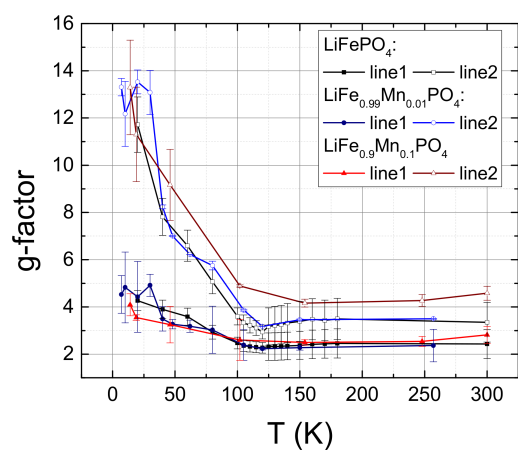


Figure 6. Temperature dependence of the g-factor of resonance signals in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$).

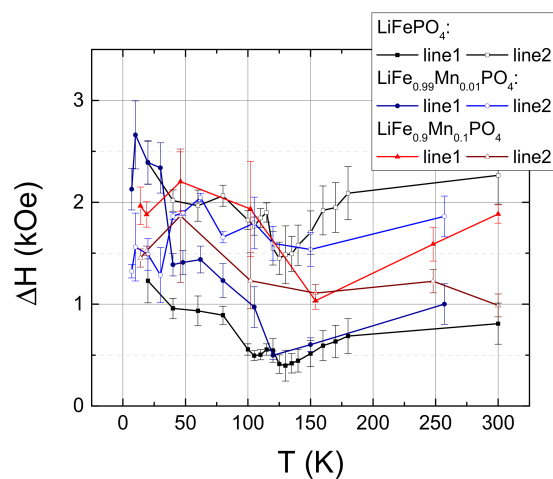


Figure 7. Temperature dependence of the ESR linewidth of resonance signals in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$).

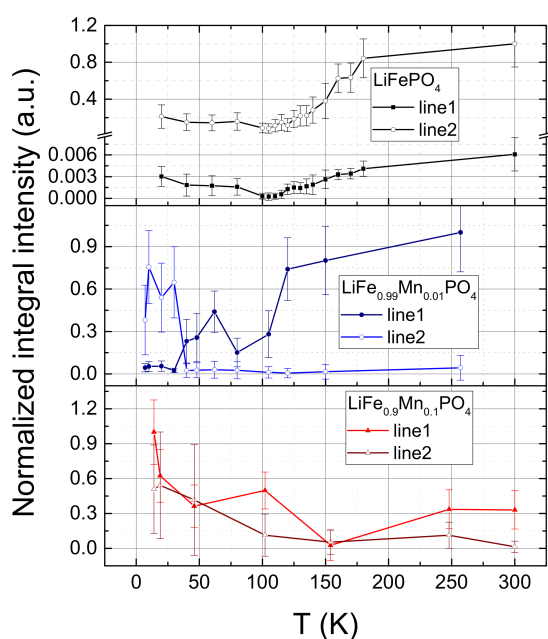


Figure 8. Temperature dependence of the normalized integral intensity of resonance signals in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$).

3. Discussion

It is necessary to start with a discussion of the nature of the ESR signals in the investigated samples. In the case of the ideal stoichiometry of LiFePO_4 , all iron ions should have the Fe^{2+} valence state and the electronic configuration $3d^6$ (5D , $L = 2$, $S = 2$). In an octahedral field, the ground orbital state of Fe^{2+} is a triplet Γ_5 if the $3d^6$ configuration is considered as one electron over a half-filled shell. Due to the spin-orbit coupling, the orbital triplet is fivefold spin-degenerated, and it splits in the triplet, quintet, and septet. The triplet is the lowest level, and its wave functions are a mixture of the eigenfunctions for the orbital moment and spin moment [25]. The absence of the fine structure of Fe^{2+} ions in the ESR spectra of $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$) can be associated with the presence of exchange interactions between the spins of iron ions. Exchange interactions between the magnetic ions in such magnetically concentrated compounds leads to the merging of the fine structure lines into a single exchange-narrowed absorption line [25].

Experimentally, the ESR spectrum of Fe^{2+} ions is difficult to detect, and it was observed in the diluted $\text{MgO}:\text{Fe}^{2+}$ system [26], where the magnesium oxide has a face-centered cubic structure and each magnesium (iron) atom is located in the octahedral oxygen environment. It was shown that the ground triplet gives rise to a first-order Zeeman splitting in an external magnetic field, and the electron spin resonance spectrum of Fe^{2+} in MgO consists of the narrow resonance line (g -factor $g = 3.428$ and linewidth $\Delta H = 10$ Oe) and broad resonance line ($\Delta H = 450$ Oe) with the same g -factor value. It was suggested that the broad resonance line in $\text{MgO}:\text{Fe}^{2+}$ is the result of the aggregation of iron ions in certain areas of the crystal that leads to the dipolar broadening of this line. The random distortions of the crystal structure in the vicinity of Fe^{2+} ions should also be taken into account [27]. The recent study of the LiMnPO_4 and LiFePO_4 systems by means of the ESR method enabled the detection of the resonance spectrum of Mn^{2+} ions, while the resonance signal from Fe^{2+} was not registered. The absence of the ESR signal from Fe^{2+} in LiFePO_4 is associated with the short relaxation times of iron ions, leading to the extreme broadening of the line [28].

Here, we suggest that we managed to observe the ESR signal due to divalent iron ions in the octahedral oxygen environment in all investigated samples. This signal is marked as line 2 in Figures 3–8 and has a g -factor of approximately 3.5 or higher (Figure 6). Because the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01, 0.1$) systems investigated here are magnetically concentrated systems, the ESR absorption linewidth is predominantly determined by the dipole–dipole and the exchange interactions between the magnetic ions. The broadening of the ESR absorption lines by dipolar interaction ΔH_{dd} was calculated using the method of moments [29] and can be estimated using the expression:

$$\Delta H_{dd}^2 = \frac{3}{5} g^2 \beta^2 S(S+1) \sum_{k=1}^N \frac{1}{r_k^6} \quad (2)$$

where g is the g -factor of the magnetic ion, β is the Bohr magneton, S is the spin of the magnetic ion, N is the number of the nearest neighboring magnetic ions, and r_k is the distance between the nearest neighboring magnetic ions. It is known from the literature [8,30,31] that the crystal structure of LiFePO_4 is orthorhombic and belongs to the $Pnma$ space group (No. 62). The lattice parameters are $a = 10.35$ Å, $b = 6.01$ Å, and $c = 4.67$ Å, the number of nearest neighboring Fe^{2+} ions is $N = 16$, and the distance between the magnetic ions varies between 3.863 Å and 6.571 Å (Figure 9). Thus, at room temperature, for $g \approx 3.5$ (Figure 6) and $S = 2$ (Fe^{2+} , $3d^6$), the estimation using Equation (2) gives the linewidth value due to the dipole–dipole interaction $\Delta H_{dd} \approx 2510$ Oe. One could expect the slight decrease in the ΔH_{dd} value, due to the decrease in the spin value S in Equation (1), if the Fe^{2+} ions are not in the high-spin state ($S = 1$). We can see that the estimated ΔH_{dd} is of the same order of magnitude as the experimental values for the initial LiFePO_4 (Figure 7); thus, there is no strong exchange interaction which can lead to the exchange-narrowing of the ESR line, as was observed in the case of the other cathode material, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ [32]. At the same

time, the estimated ΔH_{dd} is higher than the experimental values for the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0.01, 0.1$) samples (Figure 7); thus, the exchange interaction occurs and leads to the exchange-narrowing of the ESR line. The value of the exchange interaction can be estimated using the formula [33]:

$$\Delta H = \frac{\Delta H_{dd}^2}{H_{ex}} \quad (3)$$

where ΔH is the experimentally observed linewidth and H_{ex} is the exchange field. Taking into account the estimated value of $\Delta H_{dd} \approx 2510$ Oe and the average value of the experimentally observed linewidth $\Delta H \approx 1200$ Oe, one can obtain the exchange field value at room temperature $H_{ex} \approx 5.3$ kOe, which gives the exchange integral value $J \sim \mu_B \cdot H_{ex} / k_B \approx 0.4$ K, where μ_B and k_B are the Bohr magneton and the Boltzmann constant, respectively.

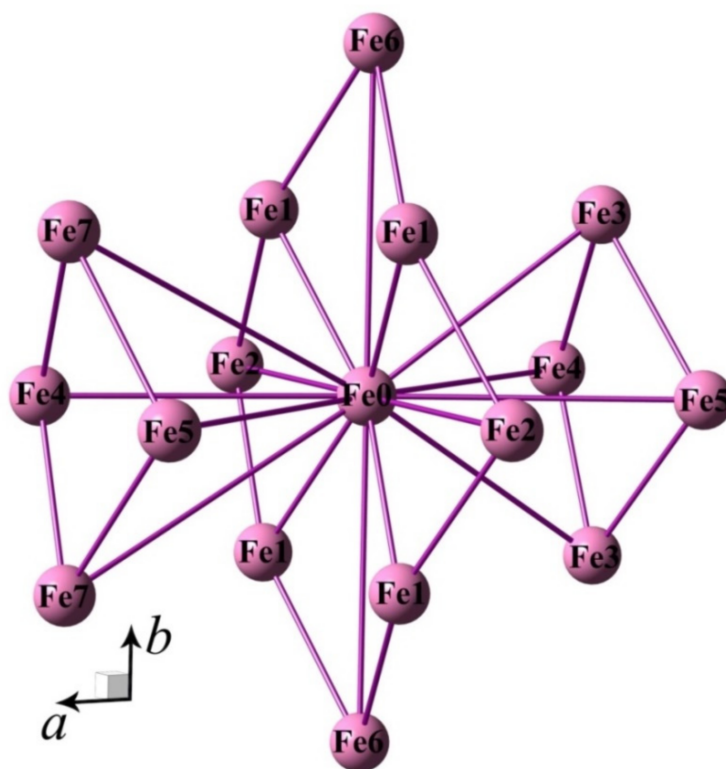


Figure 9. Crystal structure of LiFePO_4 : nearest neighboring magnetic ions for Fe^{2+} . Distances between the iron ions are: $\text{Fe0-Fe1} = 3.863$ Å; $\text{Fe0-Fe2} = 4.67$ Å; $\text{Fe0-Fe3} = 5.428$ Å; $\text{Fe0-Fe4} = 5.575$ Å; $\text{Fe0-Fe5} = 5.79$ Å; $\text{Fe0-Fe6} = 6.01$ Å; and $\text{Fe0-Fe7} = 6.571$ Å.

As regards the origin of the second line (line 1 in Figures 3–8), it is known from the literature that the single isotropic resonance line with $g = 2.245$ was detected in the ZnS:Fe^{2+} system, where the Fe^{2+} ions are located in the tetrahedral environment [26]. The experimentally observed g -factor for line 1 is close to $g = 2.245$; thus, one can suggest that the Fe ions can interchange with phosphorus ions and take their place in the PO_4 tetrahedron. However, it is more likely that this signal is observed from the magnetically correlated regions that form around (i) the Fe^{3+} ($3d^5$, $S = 5/2$) ions, which appear due to the lithium non-stoichiometry, or (ii) the Mn^{2+} ($3d^5$, $S = 5/2$) ions in $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0.01, 0.1$). The presence of iron-based superparamagnetic nanoparticles was previously evidenced in LiFePO_4 using ESR and magnetization measurements [34]. The presence of Fe^{3+} ions and the random Mn distribution in $\text{Li}_x\text{Fe}_{1-y}\text{Mn}_y\text{PO}_4$ during the initial stages of charging were evidenced using the Mössbauer spectroscopy measurements [19]. The lithium non-stoichiometry in another type of cathode material for lithium-ion batteries, leading to the appearance of mixed-valence magnetic ions, was previously detected using the ESR method [35,36].

As can be seen from Figures 1–8, the doping with manganese ions has significant effects on the ESR line shape and the temperature behavior of the ESR parameters, especially integral intensity. From Figure 1, one can see that the spectrum becomes well resolved, and the two lines in the ESR spectrum can be clearly observed with decreasing temperature from room temperature down to 100 K. Below this temperature, the linewidth increases significantly when approaching the phase transition temperature [37–39]. It is known that LiFePO_4 transforms into a collinear antiferromagnetic ground state below $T_N = 50\text{--}52\text{ K}$ [28,31,34], while FePO_4 undergoes the antiferromagnetic order at Néel temperature $T_N = 125\text{ K}$ [31,34]. One can suggest that magnetically correlated regions formed around Fe^{3+} have an ordering temperature close to that of FePO_4 ; therefore, one can see a change in the temperature dependences of all ESR parameters near this temperature (Figures 6–8). For the highest concentration of manganese in $\text{LiFe}_{0.9}\text{Mn}_{0.1}\text{PO}_4$, one can observe the increase in the ESR signal intensity with decreasing temperature, whereas in the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ ($x = 0, 0.01$) samples, the opposite behavior was observed (Figures 1 and 8). One can see that the introduction of manganese ions does not lead to the appearance of a third resonance signal in the ESR spectra, but it does change the magnitude and type of magnetic ordering in the magnetically correlated regions in the $\text{LiFe}_{0.9}\text{Mn}_{0.1}\text{PO}_4$ samples compared to the others.

4. Conclusions

ESR measurements were performed on the polycrystalline submicron carbon-coated $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ system. Two resonance signals were observed in all samples: (i) the ESR signal due to divalent iron ions in the octahedral oxygen environment, with the high value of the ESR linewidth due to the dipole–dipole interaction, and (ii) the ESR signal from the magnetically correlated regions formed near Fe^{3+} . The introduction of manganese ions does not lead to the appearance of a third resonance signal in the ESR spectra. The temperature dependence character of the integral intensity of observed resonance lines changes significantly with increasing manganese concentration, indicating a change in the nature of the magnetic interactions in the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ systems. We suggest that the noticeable capacity loss which was observed in the $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ systems when replacing iron ions with manganese ions can be explained by the random distribution of Mn ions and changes to the type of magnetic ordering in these systems, despite the attractiveness of the electrochemical $\text{Mn}^{2+}/\text{Mn}^{3+}$ pair compared with $\text{Fe}^{+2}/\text{Fe}^{+3}$. At the same time, we do not exclude the possibility that, with an increase in the concentration of Mn ions, when the percolation channels, on the basis of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ pairs, become essential, the electrochemical performance of such systems can be improved.

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