What can we learn about battery materials from their magnetic properties?

Natasha A. Chernova, Gene M. Nolis, Fredrick O. Omenya, Hui Zhou, Zheng Li and M. Stanley Whittingham*

Received 4th January 2011, Accepted 14th March 2011
DOI: 10.1039/c1jm00024a

Electrode materials for Li-ion batteries should combine electronic and ionic conductivity, structural integrity, and safe operation over thousands of lithium insertion and removal cycles. The quest for higher energy density calls for better understanding of the redox processes, charge and mass transfer occurring upon battery operation. A number of techniques have been used to characterize long-range and local structure, electronic and ionic transport in bulk of active materials and at interfaces, with an ongoing move toward in situ techniques determining the changes as they happen. This paper reviews several representative examples of using magnetic properties toward understanding of Li-ion battery materials with a notion to highlight the intimate connection between the magnetism, electronic and atomic structure of solids, and to demonstrate how this connection has been used to reveal the fine electronic and atomic details related to the electrochemical performance of the battery materials.

A Introduction

Optimization of battery performance for applications ranging from miniature hearing-aid devices to electric vehicles requires a clear understanding of the electrochemistry occurring. Li-ion batteries provide the highest energy density among known rechargeable systems, based on the light-weight shuttle ion (Li+) and insertion electrodes, such as layered transition metal oxides and olivine phosphates as cathodes and graphitic anode.1–3 Due to the limited electronic conductivity of most of the oxides and phosphates, conducting carbons and polymer binders are added to make a composite cathode.4 Nano-sized active materials are now widely used to shorten the Li-diffusion lengths and provide better power capability,5 along with doped, disordered, and amorphous materials, where defects facilitate structural changes upon lithium cycling.6–8 The structural complexity of battery electrodes presents a characterization challenge not solvable by any single technique. Therefore, to obtain a comprehensive picture, the experimental data obtained by various experimental
techniques should be brought together. In this review, we discuss one of the characterization techniques, magnetic properties, with the goal to highlight their high sensitivity to structural defects and impurities, often beyond that of X-ray diffraction.

The first clear realization of the close relation between magnetism and chemical bonding in solids, likely, goes back to the 1930s when Néel introduced local molecular field theory of antiferromagnetism and Kramers introduced superexchange, the magnetic interaction mediated by ligand orbitals (Fig. 1). The theory of superexchange was further developed by Anderson in 1950, however, it did not account for the anisotropic character of d-orbitals. It was Goodenough, who pointed out that symmetry conditions and crystal field splitting should be taken into account. Together with Kanamori, providing the theoretical base, the magnetic coupling rules were formulated for various metal–ligand–metal angles and metal electronic configurations, which are now known as Goodenough–Kanamori rules. Goodenough and Loeb provided extensive empirical proof for these rules in their work on magnetic spinels and perovskite-type manganites.

Goodenough’s discovery of two of the most commercially successful Li-ion battery cathode materials: LiCoO$_2$ in 1980 and LiFePO$_4$ in 1997 appears to be based on an understanding of the chemical bonding and electronic structure in the covalent compounds gained over the course of the research on magnetic interactions in spinels and perovskites. In this review we will demonstrate, using several examples, how the use of magnetic properties can advance the understanding of the structure, composition and electrochemical performance of Li-ion battery materials. We will also highlight the advantages and limitations of this method.

The paper is organized as follows: the main types of magnetic behaviors and basics of experimental techniques are given in the

Fredrick Omenya earned a BED (Sc.) from Kenyatta University in Kenya in 2007. He is currently a PhD student in chemistry at SUNY Binghamton in Professor M. Stanley Whittingham’s group. His research interests include synthesis and characterization of novel phosphate materials as cathodes for Li-ion batteries.

Zheng Li is currently completing his PhD under the supervision of Prof. M. Stanley Whittingham on layered oxides as cathode materials for lithium ion batteries at SUNY-Binghamton and will work as a postdoctoral research associate with Prof. Yet-Ming Chiang and Prof. W. Craig Carter on semi-solid rechargeable flow batteries in MIT. He finished his undergraduate thesis in State Key Lab of Electroanalytical Chemistry (Chinese Academy of Sciences) and received his BEng (2006) in materials physics in Jilin University (Changchun, China). Then he obtained the MEng (2008) in Tsinghua University (Beijing, China), working on lithium iron phosphate.

Hui Zhou received his BS (2003) and MS (2006) in Materials Physics from Harbin Engineering University and Shantou University, respectively. Then he joined Prof. Yanming Zhao’s group at South China University of Technology. In 2007, he obtained the State Scholarship Fund from China Scholarship Council to work in Prof. Whittingham’s group as a visiting scholar. He is currently completing his PhD in Materials Science in Prof. Whittingham’s group at State University of New York at Binghamton. His research is focused on exploring new materials, such as the metal pyrophosphates capable of two-electron transfer per redox center that he recently discovered.

M. Stanley Whittingham received his undergraduate and graduate degrees from Oxford University in the UK. He then spent 4 years in Materials Science at Stanford University, where he began a study of ion transport in solids. Following which he joined Exxon Research to embark on a study of the mechanism of the redox reduction of solids by lithium, which led to the use of intercalation compounds as battery electrodes in the mid 1970s. He returned to academia in 1988 as Professor of Chemistry at SUNY at Binghamton to build a program in Materials Chemistry. He has received the Young Author Award, the Battery Research Award and was elected a Fellow of the Electrochemical Society.
Background section. The following two sections discuss magnetic properties of layered oxides and olivine phosphates, respectively, with an emphasis on the effects of structural disorder, defects and impurities on the magnetic properties and electrochemical behavior. In conclusion, the main achievements, unresolved issues, and future research directions are summarized.

B Background

1. Basic magnetic properties of solids

When a substance is placed in an external magnetic field, \( H \), it develops magnetization, \( M \), defined as magnetic moment per unit volume. The magnetic susceptibility is defined as \( \chi = \partial M / \partial H \); it can be simplified to \( M = \chi H \) in the case of a linear \( M(H) \) dependence. \( \chi \) is dimensionless when measured per unit volume; which is cm\(^3\) in cgs units traditionally used in magnetism. It is often expressed in terms of mass units, i.e. per gram, or as molar susceptibility, \( \chi_M \), due to convenience of measurement.\(^1,2\)

Substances with negative magnetic susceptibility, the diamagnets, repel an applied magnetic field. The diamagnetic response, in classic sense, is due to the Larmor precession of electron pairs in closed atomic shells about the direction of the applied magnetic field. It results in a small, \( \chi \approx -1 \) to \(-100 \times 10^{-6} \) emu g\(^{-1}\), temperature- and field-independent contribution well described by the Pascal constants.\(^3\) Paramagnetic substances, on the other hand, have a positive magnetic susceptibility and attract an applied magnetic field. This contribution comes from the interaction of unpaired electrons with the applied magnetic field, which, in quantum-mechanical terms, is described by thermal distribution of electrons among energy levels of an atom in a magnetic field. The general equation derived by Van Vleck\(^4\) results in two types of paramagnetism: temperature-independent, also known as Van Vleck paramagnetism, which appears when the energy difference between the ground state singlet and the next excited state significantly exceeds thermal energy, and the Curie–Weiss paramagnetism, if the ground state is degenerate and there are thermally accessible excited states. The Van Vleck contribution is often found in the compounds containing d-metal ions in their highest oxidation state, i.e. with d\(^\text{8}\) electronic configuration, resulting in the susceptibility on the order of \(10^{-4} \text{ emu mol}^{-1}\). The Curie–Weiss paramagnetic behavior, described by the Curie–Weiss law, \( \chi = C/(T - \theta) \), is found in compounds containing localized unpaired electrons, such as that of d- or f-metals.

The Curie constant \( C \) is related to the number of magnetic ions \( N \) and their effective magnetic moment \( \mu_{\text{eff}} \) by \( C = N\mu_{\text{eff}}^2/3k_B \), where \( k_B \) is the Boltzmann constant. If the susceptibility is defined per mole of magnetic centers, then \( N \) is the Avogadro number, and the above equation simplifies to \( C = 1/8\mu_{\text{eff}}^2 \). It should be noted that the effective magnetic moments are not additive, therefore, if different magnetic centers are present in the compound, the average effective magnetic moment is defined as follows: \( \mu = \sqrt{x_1\mu_{\text{eff}1}^2 + x_2\mu_{\text{eff}2}^2 + \ldots + x_n\mu_{\text{eff}n}^2} \), where \( x_1, \ldots, x_n \) and \( \mu_{\text{eff}1}, \ldots, \mu_{\text{eff}n} \) are the fractions and the effective magnetic moments of different magnetic centers, respectively.

The effective magnetic moment is determined by the electronic configuration of the magnetic center. Since most of the magnetic centers in the Li-ion battery materials are d-metal ions, we will limit our consideration to this case. In solids, d-orbitals are exposed to ligand crystalline field, which lifts the degeneracy of five d-orbitals. For example, in an octahedral field, they split into three lower-energy \( t_{2g} \) and two higher-energy \( e_g \) orbitals (Fig. 1). The energy separation between \( t_{2g} \) and \( e_g \) orbitals \( \Delta \) is affected by the ligand strength. Strong field ligands cause energy level splitting \( \Delta \) to be greater than the Coulombic repulsion \( U \) resulting in low-spin complexes, where electrons favorably fill the \( t_{2g} \) orbitals with paired spins. Conversely, in high-spin complexes with weak field ligands and \( \Delta < U \), electrons fill all five d orbitals with unpaired spins (d\(^1\)–d\(^5\)) before pairing (d\(^6\)–d\(^10\)). As a result of this splitting, for many 3d complexes, orbital angular momentum, \( L \), is suppressed, or quenched. The resulting electronic states are described by spin quantum number, \( S \), only, with the effective magnetic moment \( \mu_{\text{eff}} = g\sqrt{S(S+1)}\mu_B \), where \( \mu_B = 9.274 \times 10^{-21} \text{ erg Gauss}^{-1} \) is the Bohr magneton, used as the unit, and \( g \), the spectroscopic splitting factor, which is equal to two in the spin-only case, but may depart from this value due to spin–orbit interactions.

For the orbital angular momentum to contribute, there must be a degenerate orbital of the same symmetry, allowing for an electron transfer without violation of the Pauli principle. For example, in the octahedral field case, degenerate \( t_{2g} \) orbitals have
the same symmetry, and a 90° rotation about x, y, or z axis will convert them to one another. Any t_{2g} electron configuration, except empty, half-filled, and full, allows electron transfer resulting in unquenched orbital moment. In contrast, two e_g orbitals have different symmetries and cannot contribute to orbital moment. Departure from the spin-only magnetic values is generally large for octahedral low-spin 3d^4, high-spin 3d^6 and 3d^7 configurations. The magnetic moments for such complexes may be predicted using $\mu_{\text{eff}} = \sqrt{L(L+1) + 4S(S+1)}\mu_B$. The use of the total magnetic moment, $J$, is erroneous for 3d metals, because $L$ and $S$ are not added-up to form $J$.

The Curie–Weiss temperature $\theta$ contains the information on the strength and type of the interactions between the magnetic moments, known as magnetic exchange. If the magnetic moments are well spatially separated, and cannot interact, $\theta = 0$ K, and the Curie–Weiss law is simplified to the Curie law. Positive $\theta$ indicates ferromagnetic exchange, which tends to align magnetic moments in parallel, negative $\theta$ indicates antiferromagnetic exchange. The absolute value is proportional to the sum of all the exchange integrals $J_i$ and the number of corresponding neighbors $p_i$:

$\theta = \frac{S(S+1)}{3k_B} \sum J_i p_i$. The main magnetic exchange mechanisms include, but are not limited to: (1) direct exchange, involving overlap of d-orbitals, which occurs if structure contains, for example, edge-sharing octahedra (Fig. 1); (2) the superexchange, when ligand orbitals direct spin arrangement at metal ions (Fig. 1); (3) weak dipole–dipole interactions; and (4) stronger and longer-range exchange mediated by conduction electrons, known as Ruderman, Kittel, Kasuya, Yoshida (RKKY) interaction.\(^{22}\)

It should be noted that if d-electrons in a compound are delocalized, i.e. conduction electrons, they contribute to the magnetic susceptibility differently than the localized magnetic moments described by the Curie–Weiss law. Conduction electrons exhibit temperature-independent Pauli paramagnetism as a result of “spin-up” and “spin-down” band splitting in the magnetic field, as well as diamagnetism Landau, which is $-1/3$ of Pauli contribution, leading to the total susceptibility $\chi = N_{\text{eff}}^2 k_B T_F$, where $T_F$ is the Fermi temperature (Fig. 1).

Upon lowering the temperature, ferromagnetic or antiferromagnetic long-range order may onset below the Curie $T_C$ or Néel $T_N$ temperatures, respectively. If two (or more) sublattices of an antiferromagnet bear different magnetic moments, ferrimagnetic order with net magnetic moment is established. The long-range magnetic order is often perturbed in battery materials suffering from structural disorder, defects, and frustrated magnetic interactions occurring when it is impossible to satisfy all the exchange interactions simultaneously, as in antiferromagnet on a triangular lattice. This results in either spin-glass behavior requiring both randomness and frustration, and leading to random spin configuration being frozen below the freezing temperature, $T_F$, or in cluster-glass behavior when often ferromagnetic clusters are formed, without long-range magnetic ordering.\(^{22}\)

2. Experimental techniques

In order to differentiate between these magnetic states, various $dc$ magnetization and $ac$ susceptibility tests can be performed, the standard ones being temperature and magnetic field dependences of the magnetization. The temperature dependence can tell whether the Curie–Weiss paramagnetism is observed at high temperatures and whether a magnetic ordering occurs. The magnetic field dependence can reveal the net magnetic moment formation upon ordering, as it is accompanied by change from linear to s-shaped magnetization curve, and, often, to the hysteresis of magnetization. More details on the nature of magnetic transitions can be found from the comparison of the magnetization data measured under field-cooled (FC) and zero-field cooled (ZFC) conditions. FC and ZFC susceptibility curves depart below magnetic transitions involving formation of a net magnetic moment (ferro-, ferri-) and upon spin- or cluster-glass freezing. Under ZFC conditions a random configuration of domain, or cluster, or atomic magnetic moments is frozen, while in the FC case, magnetization is larger as the net magnetic moments align with the field. It is important to use a small magnetic field when taking FC–ZFC data; 10 to 100 Oe is usually enough to produce a well-measured signal, but not to overcome the activation barrier separating the ZFC state from the FC one.\(^{23}\)

$AC$ susceptibility measured in a small, several Oe, alternating field of various frequencies provides the characteristic times of magnetic moment relaxation, which helps to distinguish between such states as spin-glass, cluster-glass, and superparamagnetism. In order to obtain the spin arrangement in an ordered phase, neutron diffraction is used. Muon spin rotation ($\mu$SR) is also used to probe the magnetic state.

C. Layered oxides

Electrochemically active LiMO$_2$ (M = Co, Ni, Mn) have the $z$-NaFeO$_2$ structure with the oxygens in a cubic close-packed arrangement (Fig. 2).\(^{24}\) Upon delithiation, the structure often becomes unstable as (a) the oxygen layers tend to shift with respect to each other as in Li$_2$CoO$_2$, where the oxygen close-packing turns hexagonal in CoO$_2$;\(^{25}\) (b) ions other than Li migrate from their sites;\(^{26}\) and (c) the compound becomes unstable at the top of charge due to the high effective equilibrium oxygen partial pressure, as in Li$_2$NiO$_2$.\(^{27}\) Therefore 100% of capacity cannot be utilized unless means of structural stabilization are found. Two main approaches include electronic stabilization and structural “pillarizing” preventing oxygen layers from sliding. Both concepts are well-demonstrated in the LiNi$_x$Mn$_{1-x}$Co$_{1-x}$O$_2$ series, where the electronic stabilization is achieved by the oxidation states of Ni$^{3+}$, Mn$^{4+}$, and Co$^{3+}$, which makes Mn electrochemically inactive, avoiding the formation of Jahn–Teller Mn$^{4+}$ upon delithiation; Ni$^{3+}$ serves as a two-electron redox center, and Co$^{3+}$ increases the electronic conductivity and layerness of the structure. At the same time, due to similar ionic radii of Ni$^{3+}$ and Li$^+$, some degree of disorder occurs and a small amount of Ni$^{2+}$ in the lithium layer (Ni$_{1.5}$) helps to stabilize the structure.\(^{28}\) We have shown that the optimum composition of these series in terms of electrochemical performance in practical voltage window is LiNi$_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$,\(^{29}\) indicating that about 4% of Ni$_{1.5}$ found in this compound is not detrimental for Li diffusion.

From the point of view of the magnetic interactions, in the ideal ccp layered structure, the transition metal (TM) layers are well separated from each other by lithium layers, so that the interlayer magnetic exchange is weak. The M–O–M angles in the
transition metal layers built of edge-sharing octahedra are close to 90°. Thus, the 90° superexchange and direct exchange mechanisms dominate the intralayer magnetic interactions. The signs and strengths of such interactions for LiNi$_{1-x}$Mn$_x$O$_2$ are summarized in Table 1 based on the Goodenough–Kanamori rules and experimental data for well-studied layered oxides such as Li$_x$MnO$_2$.\cite{28,29} If intralayer exchange is antiferromagnetic, strong geometrical frustration due to triangular arrangement of metal ions occurs resulting in complicated magnetic behavior. When Li/Ni disorder is present, the magnetic moments of the Ni$^{2+}$ ions on Li sites are coupled to those within the TM layers by 180° AF coupling to interlayer Ni$^{2+}$; the alignment of the spins in the “middle” NiO$_6$ octahedra (pale green) is not known.

LiNiO$_2$

The concept of non-stoichiometry and disorder in layered oxides goes back to the 1950s studies of lithiated NiO by Goodenough et al.\cite{30} In this work the Li$_{1-x}$Ni$_{1-x}$Mn$_x$O$_2$ series was prepared for the $0 \leq x \leq 0.483$ range with the goal of investigating their magnetic properties for possible magnetic memory applications. It was found that the compounds with high Li content could not be synthesized by solid state reaction of Li$_2$CO$_3$ and NiO; the maximum Li content achieved at 800 °C was about 0.325. The compounds with $x \approx 0.4$ were prepared in molten LiOH at 600 °C, and to achieve $x > 0.4$ excess of oxidizing agent Li$_2$O$_2$ was used. The X-ray diffraction studies revealed transition from the rock-salt cubic structure of NiO to the rhombohedral structure of LiNiO$_2$ at $x \approx 0.325$. The unit cell volume was found to change linearly according to Vegard’s law confirming a continuous solid solution. The magnetization of samples cooled to 4.2 K in 10 000 Oe field was measured, revealing non-zero magnetization above $x \approx 0.3$, which goes through the maximum at $x \approx 0.4$–0.45 (Fig. 3). The evolution of the magnetization as a function of Li content was explained by the partial ordering of Li and Ni ions in (111) planes of the cubic lattice. The antiferromagnetic spin structure of NiO was assumed, where the magnetic exchange between (111) cubic planes is antiferromagnetic, while in-plane spin alignment is ferromagnetic (Fig. 1). The assumption of the low-spin Ni$^{2+}$ produced a better fit to the data.

This model is quite similar to the one introduced by Chappel et al.\cite{31} to explain a range of FC/ZFC irreversibility temperatures observed in LiNiO$_2$ which has been a subject of numerous investigations driven by the interest in its magnetic behavior, as well as by the attempts to stabilize LiNiO$_2$ as Li-ion battery cathode.\cite{32,33} Over the course of this research it has become clear that the stoichiometric LiNiO$_2$ does not exist; it is always

Table 1 Magnetic exchange in layered LiNi$_{1-x}$Mn$_x$O$_2$: AF is antiferromagnetic and FM is ferromagnetic\cite{28}

<table>
<thead>
<tr>
<th></th>
<th>180°</th>
<th>90°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$^{2+}$–Ni$^{2+}$</td>
<td>AF very strong</td>
<td>AF strong</td>
</tr>
<tr>
<td>Ni$^{2+}$–Mn$^{4+}$</td>
<td>FM moderate</td>
<td>FM moderate</td>
</tr>
<tr>
<td>Ni$^{2+}$–Mn$^{4+}$</td>
<td>AF strong</td>
<td>FM moderate</td>
</tr>
<tr>
<td>Mn$^{4+}$–Mn$^{4+}$</td>
<td>AF strong</td>
<td>FM weak</td>
</tr>
<tr>
<td>Ni$^{2+}$–Ni$^{2+}$</td>
<td>AF strong</td>
<td>FM moderate</td>
</tr>
</tbody>
</table>

![Graph](Image)
Li-deficient and the distribution of Li\(^+\), Ni\(^{\text{3+}}\) and Ni\(^{\text{4+}}\) between lithium (3\(a\)) and TM (3\(b\)) layers is expressed as:
\[
[\text{Li}_{1-x} \text{Ni}_{\text{3+}}^x \text{Ni}_{\text{3+}}^{x'} \text{Ni}_{\text{4+}}^{x+}]_0 \text{O}_2 . \text{Ni}^{3+}\text{ at the Li site is involved in the strong } 180^\circ \text{ exchange with either } \text{Ni}^{3+} \text{ or } \text{Ni}^{4+} \text{ in the TM layer. The amount and the distribution of Ni in the lithium layer, as well as the in-layer size of the resulting ferrimagnetic clusters determine the ordering (irreversibility) temperatures and the magnetization of the resulting clusters.}

The Ni\(_{\text{Li}}\) defect is much more detrimental for the electrochemical performance of LiNiO\(_2\) than of LiNi\(_x\)Mn\(_y\)Co\(_{1-x-y}\)O\(_2\). In LiNiO\(_2\), the major redox pair is Ni\(^{\text{3+}}$/Ni\(^{\text{4+}}\), thus Ni\(_{\text{Li}}^{\text{3+}}\) can be oxidized early upon Li removal, and the small Ni\(_{\text{Li}}^{\text{4+}}\) distorts Li layers impeding the diffusion. Also, Ni\(_{\text{Li}}^{\text{4+}}\) cannot migrate from the Li layer as happens in LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\)\(^{24}\) where Li ions are found in the transition metal layer (LITM). Upon Li\(_{\text{T}}\)M removal, Ni\(_{\text{Li}}\) can go back to the TM layer and out of the Li-diffusion pathway. In this view, it is critical to control the amount of Ni\(_{\text{Li}}\) in LiNiO\(_2\), and magnetic properties have been used as a sensitive tool. In nearly stoichiometric samples, only a spin-glass-like feature near 9 K is observed,\(^{25-28}\) while in the significantly Li-deficient samples, where Ni\(^{\text{3+}}\) can cluster in the Li layer, irreversibility temperature can be as high as 240 K (Fig. 4).\(^{31-33}\) It is critical to use low-field (10 Oe) FCZFC measurements in observations of magnetic cluster ordering, as conventional fields of 1000 Oe are high enough to re-arrange the magnetization of small clusters, removing FCZFC irreversibility (Fig. 4). Such magnetic characterization works well when there is a need to compare the Li/Ni disorder within a series of samples synthesized at various temperatures or with various reagent ratios, and in combination with Rietveld refinement of the X-ray and/or neutron diffraction data. However, the absolute amount of Ni in the lithium layer is difficult to determine from the magnetization measurements alone because of the ambiguous intralayer spin ordering.

Neutron scattering studies do not reveal any clear signs of magnetic order in LiNiO\(_2\),\(^{32,35}\) therefore the intralayer spin order is not known. In both Goodenough\(^{29,30}\) and Chappel et al.'s\(^{31}\) models, a ferrimagnetic spin arrangement in Ni layers is assumed. Goodenough et al. recognized that the sign of Ni\(^{\text{3+}}$/Ni\(^{\text{4+}}\) 90° exchange is not clear from his rules due to the orbital degeneracy and competing exchange mechanisms, and took the magnetic structure of NiO as the model. Chappel et al. relied on the magnetic structure of NaNiO\(_2\). Despite of structural and electronic similarity between LiNiO\(_2\) and NaNiO\(_2\), their orbital and magnetic orderings are quite different. NaNiO\(_2\) undergoes cooperative Jahn–Teller distortion, lowering the symmetry to monoclinic, and collinear orbital ordering at 480 K.\(^{40}\) This leads to ferromagnetic in-layer exchange, which, combined with AF interlayer exchange, results in antiferromagnetic order below \(T_N = 20\) K.\(^{41}\) The Jahn–Teller distortion in LiNiO\(_2\) had been considered random\(^{42}\) until recent pair-distribution function analysis of the neutron diffraction data, which suggested local order, most likely in a trimer fashion (Fig. 4).\(^{43-44}\) The long-range order does not develop because of the strain field that the local ordering generates, and domains of about 10 nm in size are formed. Such orbital ordering is very different from that of NaNiO\(_2\) and allows both ferromagnetic and antiferromagnetic exchange.

Interesting insights into LiNiO\(_2\) magnetism in the absence of Ni\(_{\text{Li}}\) were obtained upon investigation of LiMg\(_{0.5}\)Ni\(_{1.5}\)O\(_2\), where Mg\(^{2+}\) instead of Ni\(^{2+}\) is found in the Li layer according to X-ray and neutron diffraction, as well as magnetic susceptibility data not revealing any ferrimagnetic clustering. No long-range ordering is observed in LiMg\(_{0.5}\)Ni\(_{1.5}\)O\(_2\) by muon spin relaxation, and a disordered, slowly fluctuating spin state is found below 12 K over the whole sample volume. The ESR data indicate antiferromagnetic magnons, again not consistent with ferromagnetic in-layer exchange. It is interesting to note that TiAX researchers have prepared Mg-doped LiNiO\(_2\) with excellent electrochemical properties. Their LiNiO\(_2\) doped with only 2.5% Mg delivers about 190 mAh g\(^{-1}\) at 1 C rate over tens of cycles.\(^{45}\) This confirms that the non-active Mg\(^{2+}\) is a much better interlayer pillar in LiNiO\(_2\) than the electrochemically active Ni\(^{2+}\).

Upon delithiation of LiNiO\(_2\), antiferromagnetic order was found by a \(\mu\)SR technique.\(^{46,47}\) It is counterintuitive, as Ni\(^{4+}\) with low-spin \(d^\text{6}\) configuration is expected to dilute the magnetic Ni\(^{3+}\) lattice and promote spin-glass behavior. Interestingly, similar antiferromagnetic \(\mu\)SR response is reported in LiCoO\(_2\) with isoelectronic low-spin \(d^\text{6}\) Co\(^{3+}\).\(^{48}\) The puzzles of LiCoO\(_2\) make the subject of the next section.

**LiCoO\(_2\)**

Stoichiometric LiCoO\(_2\) is an insulator with a band gap around 2.7 eV\(^{49}\) and the all low-spin Co\(^{3+}\) (3\(d^\text{6}\), \(S = 0\))\(^{50}\) is expected to show only a weak Van Vleck paramagnetism. However, the temperature dependences of the magnetic susceptibility always reveal localized magnetic moments. It has been shown that the high-temperature synthesized LiCoO\(_2\), such as that available commercially, is Li-excessive. However, the nature of charge-compensating defects and the electronic state of the Co in these compounds is still unclear.

\(^{6}\)\(^{1}\) Li NMR studies revealed the presence of paramagnetic Co\(^{3+}\).\(^{51,52}\) Delmas group also confirmed paramagnetism by the
increase of the Curie-Weiss contribution with Li excess (Fig. 5).\textsuperscript{55,56} Several defect models have been suggested. Earlier works considered Li$_{1+x}$CoO$_2$ compositions with low-spin Co$^{2+}$,\textsuperscript{51} however, no extra Li was found at the tetrahedral sites from the Rietveld refinement of the X-ray and neutron diffraction data,\textsuperscript{55} conversely, oxygen and Co deficiency was observed. Based on these data and on the similarities of the NMR spectra with Li(Ni, Co)O$_2$, which contains Ni$^{2+}$ ions isoelectronic with Co$^{2+}$, the [Li]$[\text{Co}_{1-x}\text{Li}]_x\text{O}_2\cdot\delta$ ($0 > \delta$) composition was proposed.\textsuperscript{55} Isodometric titration of Li-excess samples revealed a Co oxidation state close to 3+,\textsuperscript{56} which was also confirmed by the remarkable stability of overstoichiometric LiCoO$_2$ under elevated oxygen pressure.\textsuperscript{58} It has led to “Li$_{1+x}$Co$_{1-x}$O$_2$” model suggested by Delmas group.\textsuperscript{53} This composition implies only Co$^{3+}$, so, to explain paramagnetism, it was suggested that the Co$^{4+}$ ions next to the vacant oxygen sites have prismatic oxygen coordination resulting in intermediate spin state, $S = 1$. The intermediate-spin Co$^{4+}$ is not common, but may occur in distorted environments. For example, Co$^{3+}$ ions with magnetic moments of 3 $\mu_B$ are found at prismatic sites of Ca$_2$Co$_2$O$_6$.\textsuperscript{57} It should be noted that significant oxygen deficiency is not typical of this close-packed structure, especially if synthesized under oxygen/air. Therefore another possibility to consider is Li$_{1+x}$Co$_{1-x}$O$_2$ with low-spin Co$^{4+}$.\textsuperscript{58} It was ruled out in Delmas’ work based on the assumption that the hole in $t_{2g}$ orbital introduced by Co$^{4+}$ leads to the disappearance of the Li NMR signal, as observed upon delithiation of LiCoO$_2$.\textsuperscript{59} However, this effect might be due to the proximity of the insulator–metal transition in Li$_x$CoO$_2$, when delocalization of the hole in $t_{2g}$ orbital results in a fluctuating electronic state with such a timescale that the NMR signal is no longer observable.\textsuperscript{60} In semiconducting Li$_{1+x}$Co$_{1-x}$O$_2$, Li MAS NMR signal might still be present. Calculations of the NMR shifts are necessary to make sure that the Li$_{1+x}$Co$_{1-x}$O$_2$ model is consistent with the NMR data.

It takes long-term annealing in oxygen to obtain nearly stoichiometric LiCoO$_2$, but even those samples reveal localized magnetic moments in their temperature dependences of the magnetic susceptibility (Fig. 5). Also, about 10 vol% of antiferromagnetically ordered phase is found by the $\mu$SR below 30 K, being tentatively assigned to spin/charge fluctuations.\textsuperscript{48} Comparison of the magnetic susceptibilities of the stoichiometric samples with that of Co$_2$O$_3$ and CoO has indicated that the two oxides are present as impurities in the amount beyond the X-ray diffraction detection limit. EPR spectra, however, could not be explained by the impurities alone, and the presence of intrinsic paramagnetic surface defects, most likely, Li$^+–$O$^-$ was suggested. The antiferromagnetic phase below 30 K was not confirmed by these studies and remains a subject of controversy.\textsuperscript{62}

The electrochemical performance of LiCoO$_2$ depends on the Li content.\textsuperscript{59} Li-excessive compounds show solid-solution type behavior over the insulator–metal transition region of 0.75 $< x < 0.94$, while the stoichiometric one shows a two-phase behavior, as illustrated by the plateau in Fig. 5. Also, the Li/vacancy ordering causes a hexagonal to monoclinic structural transition at $x = 0.5$, which is the limit of LiCoO$_2$ cycling in commercial cells; it is much more pronounced in the stoichiometric sample, while the electrochemical curve of the Li-excess sample is nearly featureless in this region. Magnetic studies reveal an increased Curie–Weiss contribution upon delithiation, as well as a drop of susceptibility at 175–185 K over 0.49 $\leq x \leq 0.75$ region, attributed to the charge-ordering transition (Fig. 6). The observed effective magnetic moment suggests that low-spin Co$^{4+}$ is formed upon the delithiation.\textsuperscript{59,61,63} The report\textsuperscript{58} on high-spin Co$^{4+}$ contains an error in magnetic moment calculations;\textsuperscript{60} the data reported are actually consistent with the low-spin Co$^{4+}$, as illustrated in Fig. 7(a). Reduced values of the magnetic moment as compared to the spin-only value of 1.73 $\mu_B$ are caused by spin delocalization and transition from Curie–Weiss to Pauli paramagnetism as Li$_x$CoO$_2$ enters metallic state upon delithiation. The complex evolution of the structure, electrical and magnetic properties upon the delithiation of LiCoO$_2$ is illustrated in Fig. 7(b).\textsuperscript{64}

**Olivine phosphates**

The LiMPO$_4$ (M = Fe, Mn, Ni or Co) materials are polyanion compounds with an orthorhombic olivine structure.

![Fig. 5](image_url) **Fig. 5** Temperature dependences of the magnetic susceptibility of Li-excessive “Li$_{1+x}$CoO$_2$” and stoichiometric LiCoO$_2$ obtained from the Li-excessive sample by long-term annealing in O$_2$. The small peak just above 50 K belongs to antiferromagnetic ordering of O$_2$ trapped in the sample holder. The inset shows the electrochemical behaviour of these samples. After ref. 53.

![Fig. 6](image_url) **Fig. 6** Temperature dependences of the magnetic susceptibility of Li$_x$CoO$_2$.\textsuperscript{48} Reproduced with permission; copyright (2007) the American Physical Society.
The magnetic transition metal ions occupy the distorted octahedral M2 site forming a corner sharing MO₆ units which are separated by the PO₄ tetrahedra and edge-sharing LiO₆ octahedra (Fig. 8). This group of compounds has attractive theoretical capacity of about 170 mA h g⁻¹, however, only LiFePO₄ delivers close-to-theoretical capacity at useful current densities over extensive cycling.² LiMnPO₄ with a higher redox potential (4.1 V vs. Li/Li⁺, compared to 3.4 V of LiFePO₄) is electrochemically active only when nano, probably, because of the large difference in lattice parameters between LiMnPO₄ and MnPO₄ as well as structural distortion caused by Jahn–Teller active Mn⁶⁺⁺. The redox potentials of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ in olivine phosphates are above 5 V, and a stable electrolyte is required to utilize them as cathodes.

Olive phosphates are electrical insulators, so conductive additives or coatings are used to enhance the electronic conductivity,⁴ as a result, LiFePO₄ optimized for the electrochemical performance is not pure. Another purity issue of LiFePO₄ is caused by the air-sensitive nature of Fe²⁺, which is easily oxidized to Fe³⁺. Thus, defects associated with Fe²⁺/Fe³⁺ oxidation, as well as Fe³⁺-containing impurities are common. The synthesis of LiFePO₄ from Fe(III) precursors under reducing conditions can result in the formation of metallic iron or iron phosphide impurities.⁶⁶,⁶⁷ Iron compounds are strongly magnetic, therefore magnetic properties can be used for purity and structural quality control. The purity issues are by far less relevant in the case of LiMnPO₄, as Mn⁶⁺⁺ is the stable oxidation state. In this case structural defects, especially in the delithiated phase, are of interest. We will further focus on Liₓ(Fe₁₋ₓMnₓ)PO₄ (0 ≤ x ≤ 1, 0 ≤ y ≤ 1) series as the most relevant for current electrochemical applications.

### Magnetic structures and Fe²⁺ magnetic moment

LiMPO₄ (M = Fe, Mn) compounds are Curie–Weiss paramagnets at room temperature, and undergo antiferromagnetic phase transitions with collinear magnetic structures, but different spin orientations.⁶⁶–⁷⁰ LiFePO₄ exhibits antiferromagnetic ordering along [010], with a Néel temperature of 52 K, and LiMnPO₄ orders at 35 K along [100]. In LiFeₓ₋ₓMnₓPO₄ solid solution the Néel temperature changes linearly between the two end members; the evolution of spin alignment in the antiferromagnetic phase is unknown.⁷¹ Interestingly, FePO₄ with d⁵ Fe³⁺, same as Mn⁶⁺⁺, undergoes antiferromagnetic order at 125 K with spins aligned along a slight angle to [100] direction (Fig. 8). In Feₓ₋ₓMnₓPO₄ series the Néel temperature decreases to about 50 K at y = 0.8, the transition is getting broader with increasing Mn content, which is indicative of structural disorder.⁷¹,⁷²

There is a discrepancy in the literature concerning the effective magnetic moment of Fe²⁺ in LiFePO₄, because its high-spin \( t_{2g}e_g^2 \) \((S = 2)\) configuration allows incomplete orbital moment quenching. The spin-only effective magnetic moment is 4.9 \( \mu_B \), and if the orbital contribution is present, \( S = 2, L = 2, \mu_{eff} = 5.48 \mu_B \). The values reported for LiFePO₄ vary from 4.7 to 5.5 \( \mu_B \), with those exceeding 4.9 dominating.⁶⁶,⁶⁸,⁷⁰–⁷⁷ Hydrothermal LiFePO₄ samples synthesized in Whittingham’s group, which are X-ray pure, with the unit cell volume of 291.4 \( \text{Å}^3 \), show \( \mu_{eff} \) of 5.4–5.5 \( \mu_B \). The Fe²⁺ oxidation state in these samples is confirmed by the TGA weight gain in oxygen close to the expected 5.1%, and by X-ray absorption data (Fig. 9(c)).⁶⁶ In these calculations of \( \mu_{eff} \), \( \chi_0 = 0 \) was assumed, as the diamagnetic contribution is negligibly small and no other contributions were considered. Magnetic studies of LiFePO₄ single crystal have revealed positive and anisotropic temperature-independent contributions averaged to \( \chi_0 = 4 \times 10^{-4} \text{emu mol}^{-1} \).⁷³ With such correction, the effective magnetic moments of the hydrothermal samples are 5.2–5.3 \( \mu_B \), consistent with the single crystal average \( \mu_{eff} = 5.20 \mu_B \). It should be noted that the unit cell volume of the single crystal reported by Liang et al. is only 290.0 \( \text{Å}^3 \), it is significantly smaller than 291.4 \( \text{Å}^3 \) found in the well-ordered hydrothermal or solid-state samples or the
The magnetization curves are linear over the investigated temperature and magnetic field ranges. The deviations from such behavior are indicative of structural defects and/or impurities.

An example of a structural defect is Fe on Li site, which was observed in the single crystal study by Whittingham’s group. Li$_{0.97}$Fe$_{0.03}$PO$_4$ single crystal shows ferrimagnetic ordering due to excess Fe on Li site (Fig. 9). Similar ferrimagnetic response is reported in Li$_{1-x}$Fe$_x$NiPO$_4$ compounds below $T_N \approx 25$ K. However, Fe-excess compounds synthesized by the solid-state method do not show ferrimagnetism at 51 K. The unit cell volume of samples with 3% Fe on Li site is 291.6 Å$^3$, close to 291.66 Å$^3$ found for the Fe-excess single crystal, but much smaller than in the hydrothermal samples synthesized below 200 K, where Li/Fe disorder is assumed to explain the poor electrochemistry. The absence of ferrimagnetism and the presence of Fe$_2$P impurity in the solid-state Fe-excess samples raises the question whether extra Fe is present at Li site in these series.

The question of defects and aliovalent doping in olivine phosphates is still wide open. Clearer evidence of defects such as antisite defect, when Fe and Li switch sites, or aliovalent doping at any site is needed. Magnetic properties should be sensitive to these structural modifications; for example, dilution of the transition metal sublattice with non-magnetic ions may lead to the decrease of $T_N$ and absolute $\theta$ values. Also, depending on the concentration, non-magnetic ion dilution may disturb or destroy the antiferromagnetic order. Magnetic ions will also modify these parameters in a manner depending upon the magnetic interactions introduced. Of special interest would be magnetic properties of nano-LiFePO$_4$, where the single-phase Li cycling due to the disordered structure occurs. Initial data from the Hydro-Québec group indicate reduced effective moment of 4.7 $\mu_B$ in 35 nm nanoparticles, which is tentatively explained by the surface layer containing low-spin Fe$^{3+}$ ($S = 1$). Investigations by other techniques are required to prove this assumption. Also of interest are the magnetic interactions in Li$_x$Fe$_{1-x}$PO$_4$ compounds obtained by extrusion of Fe from Li$_x$FePO$_4$ into nano-Fe$_2$O$_3$ upon oxidation of Li$_x$FePO$_4$ in air.

The Fe-containing impurities in LiFePO$_4$ can be divided into two groups for the convenience of consideration. The first one includes the room-temperature paramagnets. These impurities modify the Curie–Weiss behavior by adding their contribution,
and introduce their own ordering transitions, if any, at lower temperatures. The most common impurity of this kind is NASICON Li$_3$Fe$_2$(PO$_4$)$_3$, which often appears in solid-state samples when Fe(III) precursors and low sintering temperatures are used. It undergoes ferrimagnetic order at $T_N = 26$ K.\textsuperscript{66} Sometimes, together with NASICON, LiFeP$_2$O$_5$ phase can be detected, which exhibits a magnetic anomaly at the same temperature range ($T_N = 27$ K). Because LiFeP$_2$O$_5$ is antiferromagnetic with smaller magnetic susceptibility than Li$_3$Fe$_2$(PO$_4$)$_3$, the magnetic susceptibility of LiFePO$_4$ samples is more sensitive to the presence of the NASICON phase.\textsuperscript{66} In addition, Fe$_2$P$_2$O$_7$ impurity was detected in the Li-deficient samples\textsuperscript{74} with a Néel temperature of 12.5 K.\textsuperscript{77}

The second, and more problematic, group of impurities includes compounds magnetically ordered at room temperature. Ferrimagnetic $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ are formed due to incomplete solid-state reaction.\textsuperscript{88} Ferromagnetic metallic iron and FeP, which orders ferromagnetically at 215 K,\textsuperscript{89} are the results of over-reduction.\textsuperscript{89} Below the ordering temperatures, these impurities show high and slightly temperature-dependent susceptibility, which is difficult to separate from the LiFePO$_4$ contribution. The Hydro-Québec group suggested separation of the Curie–Weiss LiFePO$_4$ contribution in samples with such impurities using the magnetization curves measured at various temperatures.\textsuperscript{79} This method results in less accurate determination of $\mu_{eff}$ because it involves more unknowns to fit a nonlinear magnetization of an impurity phase and simplifying assumptions, such as that the magnetization of the impurity becomes saturated in certain field. The $\mu_{eff}$ values in the range of 4.9–5.5 $\mu_B$ obtained for such impure samples are, in our opinion, within the error of the experiment and analysis method. These values should not be interpreted involving complicated physical phenomena without further evidence from other characterization techniques.

Conclusions

We hope to have shown that magnetic studies have an important role to play in the discovery and development of cathode materials for Li-ion batteries. In layered oxides, magnetic properties are used to estimate the non-stoichiometry and Li/Ni interlayer disorder. In olivine phosphates, especially LiFePO$_4$, they can be used to monitor sample purity, Fe oxidation state and its location in the structure. At the present time, quantitative analysis of these parameters from the magnetic properties alone looks challenging due to uncertainties in the electronic and magnetic states of the transition metal ions in the distorted crystalline environments of battery materials, and, also, of the magnetic interactions between them. To resolve these uncertainties, fundamental magnetic studies on well structurally characterized standard samples, preferably in a single crystal form, are needed. When the magnetic properties of the standard samples are known, the contributions from the structural defects appearing due to non-stoichiometry, disorder, or nano-sizing, as well as the effects of doping and additives would be easier to identify. As with any other methods, the experimental errors should be reasonably estimated, and the structural results suggested from the magnetic studies should be corroborated by other techniques.

Acknowledgements

Financial support by the National Science Foundation through grant DMR 0705657 is greatly appreciated. The research on olivine phosphates is supported as part of the Northeastern Center for Chemical Energy Storage, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award Number DE-SC0001294. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

References
