Solid State Nuclear Magnetic Resonance 42 (2012) 42–50

Contents lists available at SciVerse ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

NMR study of the $LiMnPO_4 \cdot OH$ and $MPO_4 \cdot H_2O$ (M=Mn, V) homeotypic phases and DFT calculations

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ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form
20 October 2011
Available online 22 November 2011

Keywords:
Lithium battery electrodes
Fermi contact
MAS NMR
DFT calculations
GGA+U
Tavorite

ABSTRACT

Following our previous work on the tavorite-like $LiFePO_4 \cdot OH$ and $FePO_4 \cdot H_2O$ phases, we report here the magnetic and NMR characterizations of analogous $LiMnPO_4 \cdot OH$, $MnPO_4 \cdot H_2O$ and $VPO_4 \cdot H_2O$ phases together with the DFT calculations of the NMR shifts. The first two compounds exhibit Curie–Weiss type magnetic behavior with Curie constants close to the theoretical ones for HS Mn^{3+}, while the vanadium compound is very close to a pure Curie-type behavior. ^7Li, ^{31}P and ^1H MAS NMR spectra are reported for the three compounds, and show strong Fermi-contact shifts for the first two nuclei, while the sign and magnitude of the ^1H shifts are very different for the three phases.

DFT calculations (FLAPW in GGA+U approximation) using the WIEN2k code and the experimental susceptibilities are shown to reproduce closely the experimental data. This situation is compared to the case of the homologous and isostructural Fe compounds, which exhibit much more complex magnetic behaviors.

1. Introduction

In the context of our work on NMR in paramagnetic battery-related materials, we recently took interest in the NMR study (^7Li, ^{31}P and ^1H MAS NMR) and in the magnetic properties for the two compounds $LiFePO_4 \cdot OH$ (tavorite) and $FePO_4 \cdot H_2O$, potential candidates for electrode materials in Li-ion batteries, and suitable materials for investigating the calculation strategies of the NMR (contact) shifts in paramagnetic compounds (high spin Fe^{3+} in both phases), a topic presently investigated by several research groups [1–3]. Taking into account the experimental magnetic susceptibility at the temperature of the NMR measurement and using the electron spin density at the nucleus obtained from FLAPW-type calculations led to rather satisfactory agreement between calculated NMR shifts and experimental ones of ^7Li, ^{31}P and ^1H for $LiFePO_4 \cdot OH$ and $FePO_4 \cdot H_2O$. However, GGA+U approximation is more appropriated for the former compound while GGA appears more suitable for the later one.

In order to analyze the relevance of such strategies, they indeed need to be applied to a broader range of materials. Since the $LiMPO_4 \cdot OH$–$MPO_4 \cdot H_2O$ family extends to other transition metals, and therefore other electronic configurations, we extend our work in the same spirit as for the Fe phases.

In the present paper, we focus on the $LiMnPO_4 \cdot OH$, $MnPO_4 \cdot H_2O$ and $VPO_4 \cdot H_2O$ phases. The structures of $LiFePO_4 \cdot OH$ and $FePO_4 \cdot H_2O$ are presented in Fig. 1 [4,5], as representative of those of the Mn and V phases. All these structures are homeotypic, and formed by chains of MO_6 (M=Fe, Mn, V) octahedra interconnected by PO_4 tetrahedra, thus forming several types of tunnels. The difference between the $LiFePO_4 \cdot OH$ and $FePO_4 \cdot H_2O$ structures resides in the distortion of FeO_6 octahedra along the chains, those being responsible for a change in the unit cell symmetry described by a triclinic (*P*-1 $LiFePO_4 \cdot OH$) or a monoclinic (*C*2/c $FePO_4 \cdot H_2O$) space group. In the case of the Fe phases, X-ray and neutron diffraction studies led to two positions for Fe in $LiFePO_4 \cdot OH$ whereas there is only one for $FePO_4 \cdot H_2O$ [4,5]. In $LiFePO_4 \cdot OH$, the Li atoms are located in the tunnels along the c axis and occupy a single site. In the two Fe phases, the P atoms occupy a single site. The H atoms in $FePO_4 \cdot H_2O$ and the one in $LiFePO_4 \cdot OH$ were shown to be bound to the oxygen atoms bridging two adjacent FeO_6 octahedra in the chains.

As mentioned, the $LiMnPO_4 \cdot OH$ and $MPO_4 \cdot H_2O$ (M=Mn, V) phases possess the same structures as the $LiFePO_4 \cdot OH$ and $FePO_4 \cdot H_2O$ ones, respectively, as described in the literature [6–13]. However, for the Mn and V phases, the hydrogens have not been localized to our best knowledge.

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doi:10.1016/j.ssnmr.2011.11.001

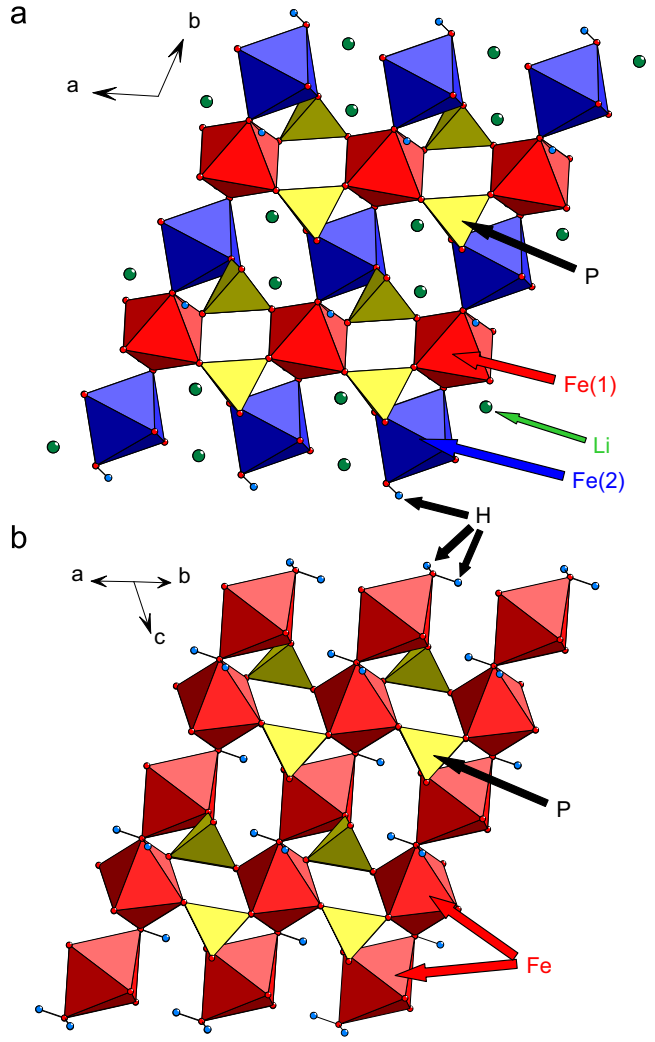

Fig. 1. Structure of (a) $LiFePO_4 \cdot OH$ (from Ref. [5]) and (b) $FePO_4 \cdot H_2O$ (from Ref. [4]).

All these paramagnetic compounds lead to NMR spectra dominated by interactions between nuclear and electron spins (hyperfine interactions). The Fermi contact shift, which governs the NMR signal of such compounds, corresponds to the presence of some density of electron spin at the nucleus probed. The sign and magnitude of the Fermi contact shift produced by this local magnetization for a given nucleus (i) can be expressed as follows [14], with the so-called contact coupling constant A^i:

$$\delta_{iso}^{i} = \frac{A^i}{\hbar} \frac{\chi_M}{\mu_0 \gamma^i g_e \mu_B} \tag{1}$$

where χ_M is the magnetic susceptibility (related to one mole of transition metal), $\hbar$ is Planck's constant, μ_0 is the magnetic permeability, γ^i is the nuclear gyromagnetic ratio, g_e is the electron g factor and μ_B is the Bohr magneton.

As described in the literature, the coupling constant is proportional to the density of electron spin at the site of the nucleus (as being transferred in effect from the various paramagnetic ions in the surrounding of the atom considered) [15]:

$$A^i = \frac{\mu_0}{3S} \hbar \gamma^i g_e \mu_B \rho^i(0) \tag{2}$$

where S is the spin quantum number of the paramagnetic ion and $\rho^i(0)$ is the spin density at or near the nucleus considered.

Therefore, the contact shift can be expressed as

$$\delta_{iso}{}^{i} = \frac{1}{3S} \rho^i(0) \chi_M \tag{3}$$

Modeling strategies enable the understanding of the electron spin transfer mechanisms based on delocalization or polarization-type mechanisms leading to positive or negative Fermi contact shifts, respectively [16]. This first approach based on plane wave/pseudo-potential calculations at 0 K with the VASP code can deal with rather large supercells. It allows (even if not quantitatively) the assignment of the different Li sites in a given compound based on the 0 K spin density found *in an ionic sphere* around Li [16–18]. Other calculation codes such as the "GIPAW package" of quantum Espresso recently proposed the use of PAW approach to provide the hyperfine coupling constant based on the spin density *at the nucleus*. From such data, Mali et al. took into account the temperature in the paramagnetic regime, assuming an ideal Curie behavior to calculate the finite temperature NMR Fermi contact shift [1]. In another recent work by Kim et al. on different phosphates, an all-electron LCAO code (Crystal06) with B3LYP hybrid exchange-correlation functional was used to calculate the spin density at the nucleus at 0 K. The authors assumed Curie–Weiss type behaviors for the materials, with experimental determination of the magnetic parameters (C, θ) for finite temperature shift calculation [2]. In their study, these authors report the difficulty to select an appropriate basis for their calculations.

In our work on the Fe phases, we first applied the pseudo-potential method earlier developed by some of us to estimate at 0 K electron spin densities at the nucleus sites. We then calculated more accurately these quantities using the full potential-LAPW code WIEN2k in the GGA or GGA+U approximation from which the finite temperature NMR shifts were obtained using the experimental magnetic susceptibility. Contrarily to an LCAO method, the Full Potential WIEN2k/LAPW method uses an adaptive basis set whose completeness can be easily evaluated, and provides an accurate description of the spin density at the nuclei of interest from which the hyperfine field (HFF) can be extracted.

In the present work, we apply the same strategy as for the Fe phases to $LiMnPO_4 \cdot OH$, $MnPO_4 \cdot H_2O$ and $VPO_4 \cdot H_2O$, i.e. magnetic and NMR characterizations, and a calculation methodology with the VASP and WIEN2k codes.

In a forthcoming paper, we will focus on understanding and describing the spin transfer mechanisms in the Fe, Mn and V phases.

2. Experimental section

$MnPO_4 \cdot H_2O$ was obtained as described by Aranda et al. [11,19]. The sample was prepared by slowly adding, at ambient temperature, H_3PO_4 (85%) to an aqueous suspension of manganese (II) carbonate hydrate with the molar ratio H_3PO_4:$MnCO_3$ of 3:1. After release of CO_2, nitric acid was added and the reaction mixture was boiled to oxidize Mn (II) to Mn (III), which resulted in the evolution of NO_2 and the formation of a dark green precipitate after one hour. The product was filtered out and dried at 80 °C overnight.

$LiMnPO_4 \cdot OH$ was obtained from $MnPO_4 \cdot H_2O$ through an H^+/Li^+ exchange as described by Aranda et al. [20]. $MnPO_4 \cdot H_2O$ was milled with an excess ($Li^+/Mn^{3+} \sim 4$) of lithium nitrate $LiNO_3$, and then the mixture was heated at 200 °C for 2 weeks. After water washing and filtration, the product was dried at 80 °C overnight.

$VPO_4 \cdot H_2O$ was prepared by hydrothermal treatment. In a typical synthesis a mixture of VCl_3, H_3PO_4 (85%) and water (molar