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# Phonons and Thermodynamics of Unmixed and Disordered $\text{Li}_{0.6}\text{FePO}_4$

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*Received: June 20, 2006; In Final Form: September 7, 2006*

The lithium-storage material  $\text{Li}_{0.6}\text{FePO}_4$  was studied by inelastic neutron scattering and differential scanning calorimetry.  $\text{Li}_{0.6}\text{FePO}_4$  undergoes a transformation from a two-phase mixture (heterosite and triphylite) to a disordered solid-solution at 200 °C. Phonon densities of states (DOS) obtained from the inelastic neutron scattering were similar for the two-phase sample measured at 180 °C and the disordered sample measured at 220 °C. The vibrational entropy of transformation is  $1.8 \pm 0.9$  J/(K mol), which is smaller than the configurational entropy difference of approximately 3.1 J/(K mol). The measured enthalpy of the disordering transition was estimated as 2.5 kJ/mol. The phonon data show a small change in lattice dynamics upon disordering.

## Introduction

A leading candidate material for positive electrodes of lithium ion batteries is olivine-type  $\text{LiFePO}_4$ . It is inexpensive, and also nontoxic and stable to oxygen loss at elevated temperature in the charged state, which give it good safety characteristics. It has a relatively high capacity of 170 mAh/g and a high discharge voltage of 3.5 V vs Li. A major problem with this cathode material is its low intrinsic electrical conductivity.<sup>1,2</sup> Much work has been done to improve the electrical performance of  $\text{LiFePO}_4$  by particle-size minimization,<sup>3</sup> carbon coating,<sup>4,5</sup> or doping with supervalent cations.<sup>6</sup> Nevertheless, the intrinsic conductivity of  $\text{LiFePO}_4$ , and methods to control it, remain topics of current interest.

When lithium ions are cyclically inserted and deinserted from this material at room temperature, a two-phase mixture is formed, of the parent triphylite phase (with composition approximately  $\text{Li}_1\text{FePO}_4$ ), and a delithiated heterosite phase (with composition approximately  $\text{FePO}_4$ ). Their relative fraction depends on the lithium content,  $x$ , in the overall material composition  $\text{Li}_x\text{FePO}_4$ . Both phases possess very similar orthorhombic structures, with the main difference being the presence of lithium chains in the triphylite structure. That, and the change in Fe–O bond length, results in a 6% contraction in the unit cell volume on formation of heterosite. Recently it was found that at elevated temperatures around 200 °C,  $\text{Li}_x\text{FePO}_4$  transforms from a two-phase mixture of triphylite and heterosite to a solid solution,<sup>7</sup> and this solid solution is a distinct phase.<sup>8</sup> Owing to the low temperatures of this phase transition, the kinetics are sluggish near the critical temperature. The disordered solid solution phase can be prepared quickly at elevated temperature, however, and will remain stable slightly above 200 °C. The thermodynamics of this unmixing/disordering phase

transition are of current interest. In the present work we performed calorimetric measurements of the enthalpy of the phase transformation, estimated the configurational entropy, and determined the vibrational entropy of the phase transition by inelastic neutron scattering.

The work was also motivated by an interest in understanding the mechanism of electrical conductivity in  $\text{Li}_x\text{FePO}_4$ .<sup>4</sup> Small polaron hopping is the expected mechanism of electrical conductivity in  $\text{LiFePO}_4$ , much as for other iron oxides. Depending on whether the iron is in the  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  valence state, its neighboring oxygen atoms are at different distances. The average Fe–O bond length for the larger  $\text{Fe}^{2+}$  ion in the triphylite is 2.172 Å, whereas it is 2.020 Å for  $\text{Fe}^{3+}$  in the heterosite. The resultant distortions accompany the motion of carrier hopping between iron ions and in fact promote the localization of charge. These relaxations of positions tend to lie along the lines between ion centers. Such displacements can be expressed as a sum of longitudinal optical phonons.<sup>9</sup> A moving electron is considered “dressed” by phonons that follow it through the material. Likewise, the presence or absence of nearby  $\text{Li}^+$  ions also causes distortions of atom positions. These distortions are generally expected to alter the frequencies of phonons, especially longitudinal optical phonons of small wavelength. The importance of this effect is not easy to predict, since it is an anharmonic effect that lies beyond most treatments of lattice dynamics and electron–phonon coupling. The present investigation by inelastic neutron scattering was performed in part to identify such changes in the phonon spectrum of disordered and unmixed  $\text{Li}_x\text{FePO}_4$ .

## Experimental Methods

A batch of  $\text{LiFePO}_4$  was prepared by a solid-state reaction consisting of a mixture of iron(II) oxalate  $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ , ammonium dihydrogen phosphate  $\text{NH}_4\text{H}_2\text{PO}_4$ , and lithium carbonate  $\text{Li}_2\text{CO}_3$  in the molar ratio (1:1:0.5). The precursors were mixed by ball milling in acetone for 12 h. The resulting gel was dried at 60 °C under vacuum, thoroughly reground,

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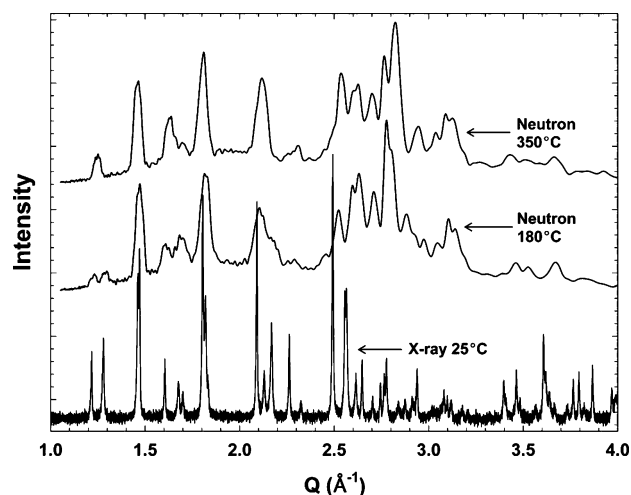
and heated under purified  $N_2$  gas for 24 h at 700 °C.<sup>10</sup> We delithiated this material chemically by use of potassium persulfate ( $K_2S_2O_8$ ) in an aqueous solution.<sup>8</sup> The  $K_2S_2O_8/K_2SO_4$  redox couple has a Nernst standard potential of approximately 5 V vs  $Li/Li^+$ , which is higher than the 3.5 V vs  $Li/Li^+$  for the  $Li_{0.6}FePO_4/Li_{1.0}FePO_4$  couple. Therefore,  $K_2S_2O_8$  can oxidize  $LiFePO_4$  to a full state of delithiation. By altering the molar ratio of  $K_2S_2O_8/LiFePO_4$ , samples with different amounts of lithium can be prepared. The composition  $Li_{0.6}FePO_4$  was selected for study in this work, as it represents an eutectoid point in the phase diagram.<sup>8</sup>

An X-ray diffractometer with Cu  $K\alpha$  radiation (Philips PANalytical X'Pert PRO X'Celerator) was used to analyze and identify the phases in the material. Samples were mixed with a silicon standard powder to ensure accuracy in peak position determinations. Rietveld analysis was used to determine phase fractions present by using Philips X'pert Plus software (PANalytical). At low temperatures  $Li_{0.6}FePO_4$  is a two-phase mixture, with nearly all the lithium in the triphylite phase ( $Li_1FePO_4$ ). The fraction of triphylite in the sample before heat treatment was determined by Rietveld analysis and was used as a measure of the concentration of lithium in the sample.<sup>8</sup>

Time-of-flight inelastic neutron scattering spectra were measured at elevated temperatures with the LRMECS chopper spectrometer at the IPNS spallation neutron source at Argonne National Laboratory. The powdered samples were encased in thin-walled Al pans and mounted on a resistively heated furnace. Spectra were acquired for the two-phase sample at 180 °C and the disordered sample at 220 °C. The two-phase sample was disordered by holding the sample at 350 °C for 3 h. White beam runs were performed at 180 °C and 350 °C to confirm complete disordering, i.e., formation of the solid solution phase. Spectra of an empty Al pan were also measured at temperature.

The detector coverage of the LRMECS spectrometer ranges from  $-7^\circ$  to  $117^\circ$ , allowing measurements over a wide range of momentum and energy transfers. The incident energy was 200 meV and the wide angular range of detector coverage allowed for momentum transfers between 0.5 and  $16.7 \text{ \AA}^{-1}$  at zero energy transfer. This corresponds to a sampling in reciprocal space over many Brillouin zones, giving a good representation of the phonon states in the material. The fwhm energy resolution was 6 meV at 150 meV positive energy transfer, and between 10 and 14 meV at the elastic line. All spectra were normalized by the total incident flux and were corrected for detector efficiency, time-independent background, and scattering from the empty sample container. The detectors were summed into 12 angle banks of approximately  $10^\circ$  in width. The elastic peak was subtracted from the spectrum in each angle bank. An iterative procedure was used to remove effects of thermal phonon occupation and multiphonon scattering from each angle bank separately.<sup>11</sup>

For pure elements of cubic crystals, this procedure for data reduction provides the phonon DOS.<sup>12</sup> For a compound with different elements, however, the result is a “neutron-weighted” phonon DOS. Because different isotopes have different cross-sections for phonon scattering in proportion to the neutron cross-section divided by atom mass ( $\sigma/M$ ), the modes with large projections onto elements of larger  $\sigma/M$  are emphasized over modes with large projections onto elements with smaller  $\sigma/M$ . For  $LiFePO_4$ , it turns out that the neutron weights for Li and Fe are fortunately nearly identical, but O scatters about 30% more strongly, and P has about half the scattering efficiency of Fe. A neutron-weight correction is not practical for the present data without information about the full lattice dynamics, but



**Figure 1.** X-ray and neutron diffraction patterns for  $Li_{0.6}FePO_4$ . The bottom curve is an X-ray diffraction pattern measured at 25 °C, the middle curve is the neutron total scattering at 180 °C, and the top curve is the neutron total scattering at 350 °C.

the experimental DOS should be correct semiquantitatively. More importantly, the trends in experimental DOS curves are sensitive to differences between samples of the same composition.

To measure enthalpies of the disordering transition, a Perkin-Elmer differential scanning calorimeter DSC-7 was used to scan samples at a 5 °C/min rate from room temperature to 500 °C. The sample was purged with argon throughout the measurements.

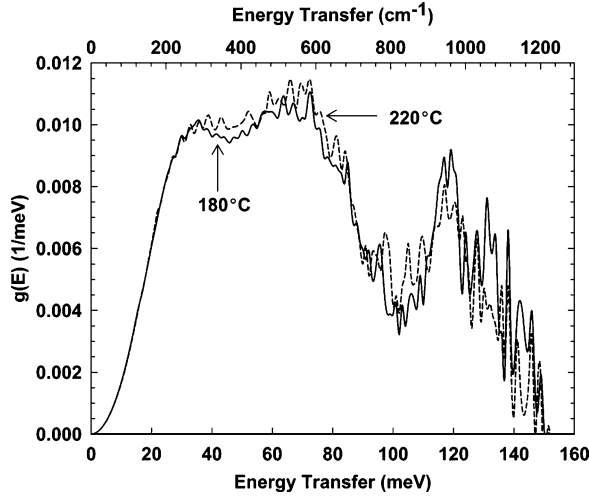
## Results

Figure 1 shows the neutron and X-ray diffraction patterns of  $Li_{0.6}FePO_4$ . The neutron data were summed from detectors at  $54.6^\circ$ ,  $82.8^\circ$ , and  $103.2^\circ$ . Diffraction peaks which have different positions in the heterosite and triphylite are apparent in the 180 °C neutron diffraction data. These peaks shift when the sample is disordered.<sup>8</sup> For example, the two peaks between  $1.2 \text{ \AA}^{-1}$  and  $1.35 \text{ \AA}^{-1}$  in the 180 °C neutron diffraction pattern have merged in the 350 °C pattern. This confirms that the sample measured at 220 °C was fully transformed to a disordered solid solution phase.

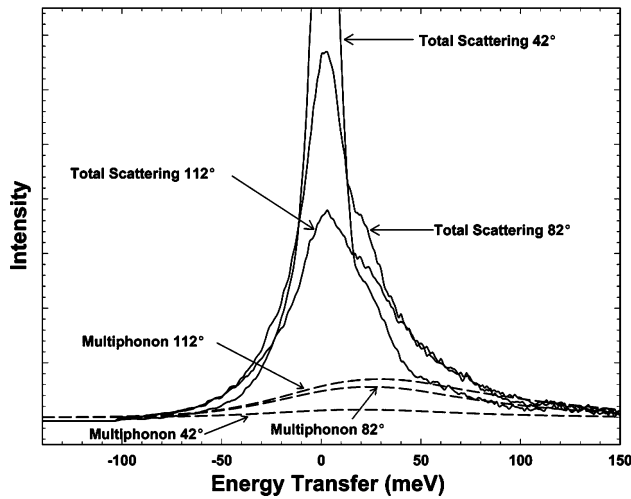
The phonon DOS curves extracted from the two-phase sample measured at 180 °C and the disordered phase measured at 220 °C are shown in Figure 2. There were some challenges in obtaining phonon DOS curves from the experimental data. The incident neutron flux was low at the energy of 200 meV, so there is some uncertainty in our selection of a cutoff energy of 150 meV. The fraction of the total scattering that is due to  $n$ -phonon processes as a function of momentum transfer,  $S_n(Q)$ , is given by:<sup>13</sup>

$$S_n(Q) = \frac{(2W)^n}{n!} e^{-2W} \quad (1)$$

where  $e^{-2W}$  is the Debye–Waller factor. The exponent,  $2W$ , increases as  $Q^2/M$ , where  $M$  is the average mass of the atoms. Thus, higher order scattering increases rapidly with momentum transferred, in particular, for light atoms such as lithium and oxygen. Further, larger scattering angles correspond to larger  $Q$ , so multiphonon scattering in the high-angle detector banks is intense. Figure 3 shows the total scattering and multiphonon scattering at 180 °C from detector banks centered at angles of  $42^\circ$ ,  $82^\circ$ , and  $112^\circ$ . Owing to excessive multiphonon scattering,



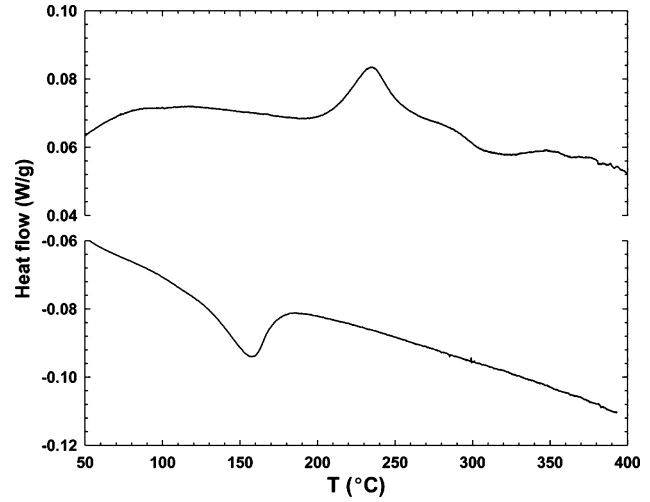
**Figure 2.** Experimental phonon DOS curves for  $\text{Li}_{0.6}\text{FePO}_4$  at 180 °C (solid) and 220 °C (dashed), normalized to unity.



**Figure 3.** Total neutron scattering spectra (solid lines) and multiphonon corrections (dashed lines) for three angle banks for the measurements at 180 °C. The detector banks were at average angles of 42°, 82°, and 112° as labeled.

the data from detectors at angles from 77° to 117° were not included in the analyses of the phonon DOS curves. The phonon DOS curves obtained from the remaining angle banks were summed to obtain the results of Figure 2. The DOS curves from the measurements at the two temperatures are surprisingly similar. The most noticeable difference is in the energy range of the optical modes, above 100 meV in this compound. The disordered sample shows a broadening of phonon modes at 120 and 130 meV compared to the two-phase sample.

The measured DSC curves are shown in Figure 4. On heating, a distinct peak in the DSC curve begins at 170 °C and ends at 320 °C. Using several independent runs, integrating this peak gave a value of  $1400 \pm 300$  J/mol. We know this number to be too small because the transformation from the two-phase to disordered state is sluggish and incomplete by 320 °C, but we were unable to resolve the enthalpy of disordering from the baseline above this temperature. To determine the fraction of sample that transformed during the DSC measurements, we performed X-ray diffraction measurements on samples that had been heated in a furnace to 325 °C and 400 °C at the same rate as the DSC measurements (5 °C/min) and then quenched to room temperature.<sup>8</sup> Analysis of the sample heated to 400 °C showed that approximately 90% of the sample transformed to



**Figure 4.** DSC scans of  $\text{Li}_{0.6}\text{FePO}_4$  from 25 °C to 400 °C. Top: heating; bottom: cooling.

the disordered phase, whereas the sample heated to 325 °C showed approximately 55% transformation. The DSC traces for heating and cooling showed a significant hysteresis.

## Discussion

**A. Thermodynamics of the Unmixing Transformation.** The configurational entropy,  $S_{\text{conf}}$ , of a disordered solid solution of solute concentration,  $c$ , can be calculated as:

$$S_{\text{conf}} = -k_B[(1 - c)\ln(1 - c) + c\ln(c)] \quad (2)$$

This simple expression from the point approximation may be appropriate for assessing the difference in configurational entropy of the disordered and unmixed  $\text{Li}_{0.6}\text{FePO}_4$ , because disordering occurs by a first-order transformation. If the disordered phase at  $\text{Li}_{0.6}\text{FePO}_4$  is a random solid solution of  $\text{Li}^+$  ions and the unmixed state has zero configurational entropy, the entropy of disordering would be 5.6 J/(K mol). If the unmixed state comprises random solid solutions of composition  $\text{Li}_{0.05}\text{FePO}_4$  and  $\text{Li}_{0.89}\text{FePO}_4$ , as has been reported recently,<sup>14,15</sup> the configurational entropy of mixing would be 3.1 J/(K mol).

Although neutron weighting causes a de-emphasis of the motions of P atoms and an overemphasis of the motions of O atoms, the phonon DOS curves for the unmixed and disordered states are surprisingly similar. Using the Planck distribution,  $n(E, T = 200 \text{ °C})$ , and the phonon DOS,  $g(E)$ , the vibrational entropy was obtained for each phase as:<sup>16</sup>

$$S_{\text{vib}} = 3k_B \int_0^\infty [(1 + n)\ln(1 + n) - n\ln(n)]g(E)dE \quad (3)$$

The vibrational entropy of disordering at 200 °C is  $1.8 \pm 0.9$  J/(K mol), a contribution smaller than the difference in configurational entropy of eq 2.

The enthalpy of transformation measured by calorimetry can be compared to the results of the equation  $T_c \Delta S_{\text{trans}} = \Delta H_{\text{trans}}$ . The phonon entropy plus the configurational entropy,  $1.8 + 3.1$  J/(K mol) predicts an enthalpy of disordering of 2.3 kJ/mol at  $T_c = 473$  K. Our direct DSC measurement gives a smaller result of  $1.4 \pm 0.3$  kJ/mol, but the sample was only 55% transformed in the temperature range where the enthalpy was measured. If we assume that the enthalpy needed to disorder the remaining 45% of the sample is equal to the enthalpy for the first portion, then we estimate a total enthalpy of the transition of approximately 2.5 kJ/mol, consistent with the



entropy results within in the error of our measurements. This is not a precise result, and we do not rule out, for example, correlations between the positions of the lithium ions in the disordered phase, or a region of diffuse interface in the two-phase mixture.

**B. Optical Phonons in LiFePO<sub>4</sub>.** Raman and IR spectra of LiFePO<sub>4</sub> show that the vibrations can be separated into two groups.<sup>17,18</sup> The first are high-frequency bands in the 1200–800 cm<sup>−1</sup> region. These are related to the stretching vibrations of the tetrahedral PO<sub>4</sub><sup>3−</sup> anion. Our results in Figure 2 suggest that these modes are present at 180 °C in the (two-phase) DOS but are damped in the 220 °C DOS. The second group is a complex pattern of bands between 700 and 50 cm<sup>−1</sup> arising from the bending vibrations of the tetrahedral group and from lattice modes. These two groups of modes correspond to regions of high intensity in the phonon DOS curves in Figure 2. The Raman and IR spectra of Li<sub>x</sub>FePO<sub>4</sub> have also been obtained as a function of lithium concentration by Burba and Frech.<sup>19</sup> These authors argue that, because the lithium ions are coordinated to oxygen atoms, which are in turn covalently bonded to phosphorus, the vibrations of the phosphate groups are expected to be extremely sensitive to the presence of lithium ions.

The salient result of Figure 2 is that the phonon DOS curves of the unmixed and the disordered samples are surprisingly similar at low energies but not at high energies. The low energy modes (below 35 meV or 300 cm<sup>−1</sup>) are expected to be primarily acoustic lattice modes, involving translatory and librational motions of the PO<sub>4</sub><sup>3−</sup> ions and translatory motions of the Fe<sup>2+</sup> ions. There is perhaps a difference in the modes between 35 and 85 meV, but this is small. These modes include the PO<sub>4</sub><sup>3−</sup> bending modes and some modes from lithium motions.<sup>19</sup> The largest difference between samples is found in the region of the high-energy optical modes between 100 and 150 meV. The structure of the DOS around 120 and 130 meV is less distinct in the disordered sample. This could be caused by small-scale heterogeneities in the disordered material, presumably on a dimension characteristic of the wavelengths of the vibrations. For example, disorder in the Li<sup>+</sup> ions could cause a spread of the vibrational frequencies. Alternatively, damping could cause the loss of structure in the optical modes. This does not occur in the lower-frequency parts of the spectrum, suggesting that the damping mechanism is specific to optical modes. A damping mechanism could originate from the motion of Li ions, charge hopping between Fe ions, or some combination of these dynamic processes, although the present results do not justify definitive statements about these processes.

## Conclusions

Inelastic neutron scattering measurements were performed at elevated temperatures to obtain phonon densities of states of

two-phase and disordered Li<sub>0.6</sub>FePO<sub>4</sub>. The DOS curves were used to obtain a difference in vibrational entropy between the two-phase and disordered samples of  $1.8 \pm 0.9$  J/(K mol), which is smaller than the difference in configurational entropy of 3.1 J/(K mol). Both types of entropy are larger in the disordered phase. From calorimetry measurements on partially transformed samples, we estimate the enthalpy of mixing as 2.5 kJ/mol, approximately consistent with the vibrational and configurational entropies of mixing. The differences in the phonon DOS curves of the two-phase and disordered materials were small, but there was some reduction in sharpness of optical modes in the disordered sample that could be related to differences in dynamical processes in the disordered phase.

**Acknowledgment.** The authors thank Dr. Khalil Amine, Dr. Ilias Belharouak, and Argonne National Laboratory for providing the LiFePO<sub>4</sub> material. This work was supported by the Department of Energy through the Basic Energy Sciences Grants DE-FG03-00ER15035 and BES-MS, W-31-109-ENG-38, and by the National Sciences and Engineering Research Council of Canada through a Discovery grant.

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