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Unusual Mössbauer phenomenon in Li_xFePS_3

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Lithium intercalation in layered (two-dimensional) $FePS_3$ was studied by ^{57}Fe Mössbauer spectroscopy, which shows the presence of two iron sites Fe(A) and Fe(B) for the Li_xFePS_3 ($x \neq 0$) system. The Mössbauer characteristics of the Fe(A) site remain almost identical to those of the iron site in the host $FePS_3$. The Mössbauer peaks of the Fe(B) site, which corresponds to the reduced iron, increase with lithium intercalation. The smaller isomer shift found for the Fe(B) site is peculiar in the light of all known previous Mössbauer data, and has been attributed to a greater overlap distortion of core orbitals and/or to a greater $4s$ electron population on the Fe(B) site than on the Fe(A) site. According to the relative intensity of the Fe(B) site as a function of lithium intercalation, the Fe(B) site is apparently consistent with a zero-oxidation-state iron atom.

I. INTRODUCTION

It is known from several recent studies that intercalation of electron-donor species (e.g., alkali and post-transition-metal elements) in layered compounds leads to charge transfer from the intercalated atoms to the host lattice. This charge transfer induces a wide range of changes in the magnetic, electrical, optical, and thermal properties of the host materials. Such property changes have been the subject of numerous experimental and theoretical studies.[1-6] During the course of our recent investigation of Li_xFePS_3 by Mössbauer spectroscopy, we observed a Mössbauer behavior of iron remarkably different from that observed for other intercalated iron compounds. In the present study we report this unusual Mössbauer property of Li_xFePS_3 and discuss its probable origin.

II. USUAL EFFECT OF INTERCALATION ON MÖSSBAUER ISOMER SHIFT

The magnetic, transport, and spectroscopic properties of various intercalated layered compounds[6-25] reveal the occurrence of charge transfer in those compounds, which is evidenced by the phenomenon associated either with electron filling of the metal cations or with electron removal from the intercalating species. To a first approximation, all the experimental results on these compounds are considered as consistent with a rigid-band model, in which electron transfer from intercalating species is believed to increase the electron occupancy of the d-block bands of the host lattice without strongly modifying its structure.[1-6]

From Mössbauer data on intercalated iron compounds, one can study how charge transfer affects the filling of Fe $3d$ levels on the basis of the ^{57}Fe isomer shift. Table I summarizes the available Mössbauer results on intercalated oxides, chalcogenides, and halides. Inspection of this table reveals that electron transfer to iron (i.e., reduction of iron) is always reflected by an increase of its isomer shift, δ. For ^{57}Fe the $\Delta\langle R^2\rangle$ value is negative, so that δ increases if the electron density at the nucleus $\rho(0)$ decreases. The increase of δ with reduction of iron can be easily understood: Upon increasing the number of $3d$ electrons, the $3s$ electrons of Fe are better screened so that the $3s$ orbital χ_{3s} becomes more expanded. This leads to a decrease in $\rho_{3s}(0) = |\chi_{3s}(0)|^2$, and hence to an increase of δ. This general trend is applicable to all the compounds of Table I. These compounds contain iron atoms of high oxidation state (greater than 2), so that the isomer shifts of the unintercalated materials are in the range of 0.3 ± 0.1 mm/s.

III. MÖSSBAUER RESULTS OF Li_xFePS_3 ($0 \leq x \leq 1.45$)

A. Reduction sites of $FePS_3$

$FePS_3$ consists of Fe^{2+} cations ($\delta = 0.86$ mm/s at room temperature) and $P_2S_6{}^{4-}$ anions. In spite of their layer structures and empty sites present in their van der Waals gaps,[26] the MPS$_3$ phases were not considered feasible for lithium intercalation for many years since it was difficult to imagine reduction of Fe^{2+} to a lower oxidation state. However, several studies have shown that alkali metal, organometallic, and organic donors can intercalate the $FePS_3$ compounds.[27-30] In fact, the MPS_3 (M = Ni,Fe)/Li electrochemical system shows theoretical characteristics similar to that of the well-known TiS_2/Li. These experimental results led to the following question: What are the reduction sites of the $FePS_3$ system? Several empty orbitals of $P_2S_6{}^{4-}$ ions were suggested as acceptor levels of $FePS_3$ in the past,[31] but it is now clear that partially filled $3d$ levels of Fe^{2+} are responsible for intercalation in $FePS_3$.[32] The presence of high spin Fe^{2+} ions in $FePS_3$ was shown by Brec *et al.*,[33] who also reported that the magnetic properties of Li_xFePS_3 hardly differ from those

TABLE I. Summary of available Mössbauer spectroscopy data on intercalated iron compounds. These results show that reduction of the host iron upon charge transfer leads to an increased isomer shift (δ denotes the isomer shift in mm/s relative to the metallic iron at 300 K). (HS denotes high spin and LS denotes low spin.)

Compound	Variation of δ with x	Reference
Li_xFeCl_4	δ increases from 0.22 for $x=0$ (Fe^{3+} HS) to 1.1 for $x=2$ (Fe^{2+} HS). Multisite spectra reflecting intermediate valencies Fe^{m+} $(2<m<3)$ for $1<x<2$.	42
$Li_xFeV_3O_8$	Small increase of δ when x increases ($\delta\simeq 0.40$, Fe^{3+} HS).	43,44
Li_xFeS_2	δ increases from 0.30 ($x=0.14$) to 0.50 ($x=2$). δ is also higher for $x=2$ than for the $LiFeS_2$ sample prepared at high temperature from the elements.	45—47 48,49
Li_xKFeS_2	$\delta=0.22$ for $x=0$ (Fe^{3+} HS). Presence of iron sites with intermediate valency Fe^{m+} $(2<m<3)$ for $x=1$ $(0.22<\delta<0.54)$	39,50
$Li_xFe_{0.1}V_{0.9}S_2$	$\delta=0.297$ for $x=0$ (Fe^{2+} LS). $\delta=0.592$ for $x=1$ (Fe^{2+} HS). The transition LS$\rightarrow$HS occurs at about $x=0.75$.	51,52
$Li_xFe_{1.33}Nb_{2.67}Se_{10}$	$\delta=0.37$ for $x=0$. Appearance of Fe^{2+} atoms for $x\neq 0$ ($\delta\simeq 1.1$).	53
FeOCl (krypton 22) FeOCL (krypton 21)$_{1/18}$	Simultaneous presence of Fe^{3+} and Fe^{2+} at $T\leq 140$ K. The Fe^{2+} site is due to the charge transfer from the intercalated molecule to the host FeOCl lattice.	54,55
FeOCl (α-picoline)$_{0.25}$	Presence of Fe^{3+} ($\delta=0.42$) and Fe^{2+} ($\delta=1.07$) at $T\leq 230$ K. Charge transfer from picoline to the Fe^{3+} ions.	56
$FeOCl(FeCp_2)_{1/6}$	Presence of Fe^{2+} at 77 K due to charge transfer from $FeCp_2$ to FeOCl.	57

of $FePS_3$. However, recent studies on Li_xFePS_3 show a small decrease in the magnetic susceptibility of Li_xFePS_3, with respect to that of $FePS_3$, upon increasing x.[7] This discrepancy between the two studies[7,33] concerning the magnetic susceptibility of Li_xFePS_3 resulted largely from the slow process of electron transfer in Li_xFePS_3. Consequently, as pointed out by Whangbo *et al.*[32] based upon their band electronic structure calculations on $FePS_3$, electrons donated by Li in Li_xFePS_3 must go into the empty $3d$ levels of Fe^{2+}, thereby creating highly reduced iron species.

B. Experiments

The Mössbauer spectra of Li_xFePS_3 $(0\leq x\leq 1.45)$ were obtained with a conventional transmission spectrometer from ELSCINT Inc. with the following characteristics: source, Co^{57}(Rh) of ~24 mC; experimental full width at half maximum (FWHM) of a sodium nitroprusside (SNP) absorber, 0.226 mm/s. Li_xFePS_3 samples were prepared by the n-butyl-lithium technique at room temperature, and were analyzed for their lithium contents using flame spectrophotometry. Previous electrochemical and x-ray diffraction studies showed that the Li_xFePS_3 phases are

TABLE II. Hyperfine Mössbauer parameters for Li_xFePS_3 at room temperature δ denotes the isomer shift relative to the metallic iron at 300 K (error is ± 0.01). ΔE denotes the quadrupole splitting. FWHM denotes the full width at half maximum. The relative intensity for each iron site has an error of $\pm 2\%$).

x	Site	δ (mm/s)	ΔE (mm/s)	FWHM (mm/s)	Relative intensity
0	Fe(A)	0.86	1.52	0.29	100
	Fe(B)				
0.50	Fe(A)	0.87	1.55	0.27	75
	Fe(B)	0.47	0.52	0.64	25
0.83	Fe(A)	0.87	1.56	0.27	65
	Fe(B)	0.45	0.53	0.68	35
1.11	Fe(A)	0.86	1.55	0.26	60
	Fe(B)	0.44	0.52	0.54	40
1.45	Fe(A)	0.86	1.55	0.25	52
	Fe(B)	0.43	0.48	0.51	48

homogeneous up to $x \simeq 1.45$,[26,34] and thus the lithium concentration range $0 \leq x \leq 1.45$ was examined in the present study. All the Mössbauer spectra of $\mathrm{Li}_x\mathrm{FePS}_3$ were fitted with free parameters, and the fitting routine employed Lorentzian line shapes. The quadrupole splitting ΔE is equal to the absolute value of $\frac{1}{2}eV_{zz}Q(1+\eta^2/3)^{1/2}$, while the isomer shift δ is relative to iron metal at ambient temperature.

C. Results and discussion

The Mössbauer spectra of $\mathrm{Li}_x\mathrm{FePS}_3$ obtained at room temperature are summarized in Fig. 1. For FePS_3 a quadrupole doublet is observed with quite a narrow line (FWHM equals 0.29 mm/s). The δ and ΔE values of FePS_3, shown in Table II, are in agreement with the previous results.[35,36] The iron responsible for the Mössbauer spectrum of FePS_3 may be referred as Fe(A). Figure 1 and Table II show that for $x \neq 0$ there are two kinds of iron states in $\mathrm{Li}_x\mathrm{FePS}_3$. One is Fe($A$), and the other iron, which will be referred to as Fe(B), has a doublet with δ and ΔE values smaller than those of Fe(A). The relative intensity of the peaks associated with Fe(B) sites increases with x. The left-hand-side peaks of the two doublets are very close to each other, so that the two major peaks of $\mathrm{Li}_x\mathrm{FePS}_3$ increase their asymmetry as x increases.

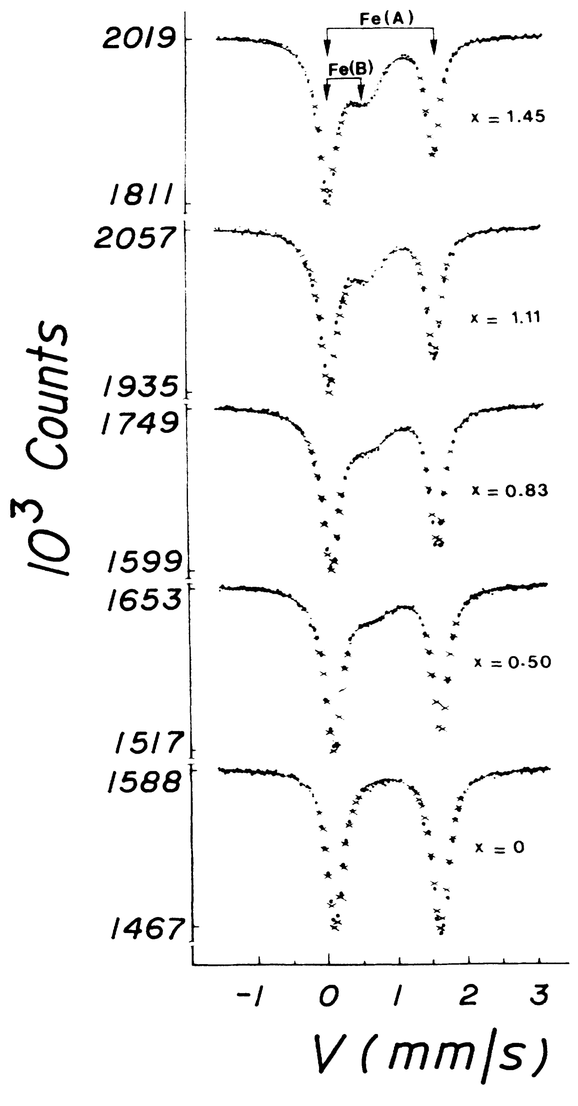

FIG. 1. Mössbauer spectra for $\mathrm{Li}_x\mathrm{FePS}_3$ at room temperature. The Fe(A) doublet, present in all spectra, is that of the host compound FePS_3. The Fe(B) doublet is present only in the intercalated compounds ($x \neq 0$) and increases when x increases. The zero velocity is the center of the metallic iron spectrum at room temperature.

The Fe(B) site occurs only when $x \neq 0$, and its Mössbauer peaks increase their intensity as x increases. Thus, the Fe(B) site is attributed to a reduced iron site expected as a result of intercalation. The isomer shift δ of the Fe(A) site remains very much the same (~ 0.86 mm/s) throughout the whole range of x. The Fe(B) site, i.e., the reduced iron site, does not have a greater but a smaller isomer shift (~ 0.45 mm/s) than does the starting Fe(A) site. According to the general Mössbauer trend discussed in Sec. II, the reduced site Fe(B) appears to have a higher oxidation state than does the unreduced site Fe(A). It is further noted from Table II that, at least in the initial stage of intercalation, about two lithium atoms are needed to produce one Fe(B) site as if the oxidation state of Fe(B) is zero. In a simple molecular-orbital model that incorporates the locally octahedral environment of Fe^{2+} in FePS_3, the electronic configuration of Fe(B) may be described as $(t_{2g})^6(e_g)^2$.

As discussed already in Sec. II, the usual trend that δ increases upon reduction is easily explained by the observation that reduction of iron leads to an increased screening of the $3s$ electrons and hence to a decreased $\rho_{3s}(0) = |\chi_{3s}(0)|^2$. This conclusion, essentially based upon free-ion Hartree-Fock atomic-orbital calculations, is consistent with the experimental results on strongly ionic compounds, fluorides, and oxides.[37] Therefore, for those compounds, other factors that decrease the isomer shift upon reduction are relatively unimportant compared with the screening effect of the $3d$ electrons upon the $3s$ orbital.

For iron sulfides, in which the extent of covalent bonding is more significant than in the oxide and fluorides, it is difficult to assign their iron ionization states, m. Further the values of their isomer shifts show some variation.[38] Nevertheless, a linear relationship (i.e., $\delta = A - 0.52m$) was found between δ and m ($2 \leq m \leq 3$) for most octahedrally ($A = 1.85$) and tetrahedrally ($A = 1.68$) coordinated irons.[39] It is noted that, in iron sulfides, the observed maximum δ value is close to 0.9 mm/s, the value corresponding to octahedral ferrous compounds with well-localized $3d$ electrons such as FePS_3, $\mathrm{FeIn}_2\mathrm{S}_4$, and $\mathrm{Fe}_{0.56}\mathrm{Ta}_2\mathrm{S}_4$.[38] δ values greater than 0.9 mm/s, which might be attributed to lower oxidation states of iron, have never been observed. It is obvious that the linear relationship, $\delta = A - 0.52m$, is not applicable to our data on $\mathrm{Li}_x\mathrm{FePS}_3$. Consequently, it is necessary to reexamine the factors such as overlap distortion of core orbitals and $4s$ orbital participation in bonding that can decrease δ upon reduction of iron. Certainly, those factors are a complicated function of the iron-sulfur distance, the extent of covalent interaction between iron and sulfur, etc.[40]

In our phenomenological approach, it may be assumed that reduction of Fe(*A*) to Fe(*B*) in Li_xFePS_3 involves only the populations of the $3d$ and $4s$ orbitals. According to results of Walker *et al.*,[41] the decrease of δ from ~ 0.85 mm/s for Fe(*A*) to ~ 0.45 mm/s for Fe(*B*) corresponds to the change in a free-iron configuration from $3d^6 4s^{0.2}$ to $3d^7 4s^{0.8}$. As pointed out already, the increased $3d$ orbital population would increase δ via its screening effect upon the $3s$ orbital. Thus the decrease of δ on going from $3d^6 4s^{0.2}$ to $3d^7 4s^{0.8}$ is due to the increased $4s$ orbital population, whose effect must dominate over the $3d$ orbital screening effect. The iron $3d$ orbitals would be more extended in a crystal with substantial covalent bonding than with strong ionic bonding. Thus the isomer shift of the former would be less sensitive to a change in the $3d$ orbital population: in fact, for the reduction of Fe^{3+} to Fe^{2+}, the increase of δ is ~ 0.4 mm/s for iron sulfides but ~ 1.0 mm/s for strongly ionic compounds.[39]

Another factor to consider is overlap distortion of core orbitals, which is known to strongly influence the isomer shift. In the case of octahedrally coordinate iron oxides, the charge density increase $\Delta\rho_{ov}(0)$ due to overlap distortion can be as large as twice that expected on adding one $3d$ electron to Fe^{2+} [i.e., $\Delta\rho(0) \simeq 1$ a.u. on going from $3d^6 4s^x$ to $3d^7 4s^x$ for $0 \le x \le 0.3$].[40,41] Thus the isomer shifts of Fe(*A*) and Fe(*B*) in Li_xFePS_3 suggest that a stronger overlap distortion of core orbitals takes place on Fe(*B*) than on Fe(*A*), which could be due to the geometry change around Fe(*B*) upon reduction.

In order to examine how the $4s$ orbital density $\rho_{4s}(0)$ and the coordinate geometry of octahedral iron are affected by the $3d$ orbital population, we carried out extended Hückel molecular orbital[58] (EHMO) calculations on octahedral complex $Fe^{x+}(S^{2-})_6 = FeS_6^{x-12}$ as a function of Fe-S distance and the oxidation state $x(=0,2,3)$. The atomic parameters of Fe and S were taken from the work of Whangbo *et al.* on $FePS_3$.[32] In EHMO calculations, the total energy E_{tot} of FeS_6^{x-12} is given by the sum of all the occupied molecular-orbital (MO) energies e_i,

$$E_{tot} = \sum_i n_i e_i \,, \tag{1}$$

where the MO occupation number $n_i = 1$ or 2. For the iron with high spin configuration, the octahedral complex FeS_6^{x-12} has two, four, and five singly occupied ($n_i = 1$) d-block MO's. Figure 2 summarizes the total energies of FeS_6^{x-12} as a function of the Fe-S distance d. The energy minima occur at $d = 2.595$, 2.645, and 2.700 Å for $x = 3$, 2, and 0, respectively. The increase of the Fe-S distance upon reduction is an expected trend. The electron density of the $4s$ orbital χ_{4s} at the nucleus can be written as

$$\rho_{4s}(0) = \sum_i^{\text{occ}} n_i (C_{4s,i})^2 \, |\chi_{4s}(0)|^2$$
$$= P_{4s,4s} \, |\chi_{4s}(0)|^2 \tag{2}$$

with

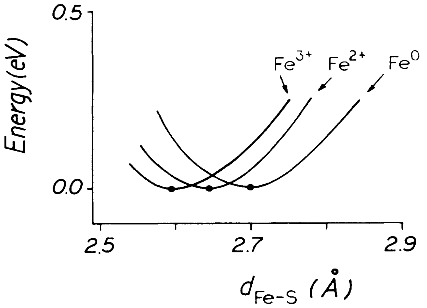

FIG. 2. Total energy of FeS_6^{x-12} ($x = 0,2,3$) for an iron with high spin configuration calculated as a function of Fe-S distance. For each potential-energy curve, the ordinate presents the relative energy in eV. For $x = 3$, 2, and 0, the energy minimum of FeS^{x-12} occurs at $d_{Fe\text{-}S} = 2.595$, 2.645, and 2.700 Å, respectively.

$$P_{4s,4s} = \sum_i^{\text{occ}} n_i (C_{4s,i})^2 \,,$$

where $C_{4s,i}$ is the coefficient of χ_{4s} in the MO ψ_i. Thus Eq. (2) shows that, in FeS_6^{x-12} (and in other sulfides as well), the magnitude of $\rho_{4s}(0)$ depends upon two factors, the net population of the $4s$ orbital $P_{4s,4s}$ and $|\chi_{4s}(0)|^2$.

EHMO calculations are based upon Slater-type atomic orbitals, for which χ_{4s}^{STO} is given by

$$\chi_{4s}^{STO} = N r^3 \exp(-\xi r) \,, \tag{3}$$

where ξ and N are the orbital exponent and the normalization constant, respectively. Since $\chi_{4s}^{STO}(0) = 0$, it is impossible to obtain the $|\chi_{4s}(0)|^2$ value expected for the $4s$ orbital of hydrogenic atomic-orbital type.[59] Thus we will only examine how the $\rho_{4s}(0)$ value is affected by $P_{4s,4s}$. The bottom curve of Fig. 3 shows the $P_{4s,4s}$ values calcu-

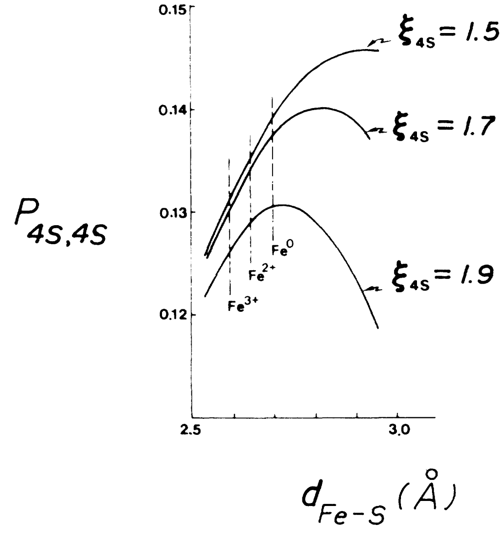

FIG. 3. Calculated $P_{4s,4s}$ values of FeS_6^{x-12} as a function of the Fe-S distance for the orbital exponents $\xi_{4s} = 1.5$, 1.7, and 1.9.

lated for FeS_6^{x-12} as a function of the Fe-S distance d. When we take these $P_{4s,4s}$ values corresponding to the optimum Fe-S distance of the FeS_6^{x-12} complexes for $x=3$, 2, and 0 it is obvious from Fig. 3 that reduction of iron increases the $P_{4s,4s}$ value, which is a factor that would increase the $\rho_{4s}(0)$ value according to Eq. (2). As in the case of the $|\chi_{3s}(0)|^2$ value, the $|\chi_{4s}(0)|^2$ value might decrease as the iron is progressively reduced since the increase of the $3d$ orbital population would make the $4s$ orbital more diffuse. As already mentioned, we cannot evaluate the change in the $|\chi_{4s}(0)|^2$ value in our calculations. Nevertheless, it is reasonable to suppose that, for the $\rho_{4s}(0)$ value to increase upon reduction despite the opposing effect of $|\chi_{4s}(0)|^2$, the extent of the $4s$ orbital participation in bonding and hence the $P_{4s,4s}$ value should increase when the $4s$ orbital becomes more diffuse. This hypothesis was tested by repeating EHMO calculations on FeS_6^{x-12} with more diffuse $4s$ atomic orbitals (i.e., with orbital exponents $\xi_{4s}=1.7$ and 1.5, reduced from the value $\xi_{4s}=1.9$). The upper two curves of Fig. 3 show the calculated $P_{4s,4s}$ values of FeS_6^{x-12} as a function of the Fe-S distance for $\xi=1.7$ and 1.5. In agreement with the above-mentioned hypothesis, the $P_{4s,4s}$ values are found to increase when the $4s$ orbital is made more diffuse.

IV. CONCLUDING REMARKS

Our Mössbauer studies on Li_xFePS_3 show the presence of two iron sites Fe(A) and Fe(B) for $x \neq 0$. The Mössbauer characteristics of the Fe(A) site are almost identical to those of the iron site in $FePS_3$. The Mössbauer peaks of the Fe(B) site, absent when $x=0$, increase their intensity with lithium intercalation. Therefore the Fe(B) site is identified as an iron site reduced from Fe(A) upon intercalation. In contrast to the typical Mössbauer trend established for strongly ionic compounds, the reduced site Fe(B) is found to have a smaller isomer shift than does the unreduced site Fe(A). This anomalous phenomenon may be attributed to a greater overlap distortion of core orbitals and/or to a greater extent of $4s$ orbital participation in bonding on the Fe(B) site than on the Fe(A) site, which might eventually originate from the presence of substantial covalent bonding between iron and sulfur. The results of our EHMO calculations on model complex FeS_6^{x-12} are consistent with the above picture. The initial stage of intercalation in Li_xFePS_3 shows that above two lithium atoms are required to create one Fe(B) site, as if the oxidation state of Fe(B) is zero. Determination of the exact nature of the Fe(B) site is the subject of our work in progress.

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