Electrical conductivity of lithium-intercalated thiophosphate NiPS$_3$ single crystals

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Conductivity measurements were made on lithium-intercalation complexes Li$_x$NiPS$_3$ both during the intercalation process and after the intercalation has ceased. The intercalation process was characterized by means of the conductivity measurements as a function of the intercalation time. Results for equilibrated samples are presented as a function of both the temperature and the lithium concentration. An overall and quick increase in the electrical conductivity, a contemporaneous decrease in the activation energy, and a degenerate semiconducting behavior at high lithium contents were observed. All these effects suggest that, with respect to the pure NiPS$_3$, a new conduction mechanism occurs at a different energy level from the very beginning of the intercalation process. Taking the probable nickel reduction into account, a possible identification of the lithium 2s electron-accepting levels is proposed. In the early intercalation times a simple empirical model is formulated to correlate the data as a function of the intercalation time and as a function of temperature.

INTRODUCTION

The lithium-intercalation complexes of the transition-metal thiophosphates Li$_x$MPS$_3$ are formed when lithium is inserted in their van der Waals gaps. The intercalation may often induce rather dramatic changes in the physical properties of these host lattices. In fact, the intercalation process, which is usually accompanied by a charge transfer from lithium to the host layer, may be used to "fine-tune" the electronic properties of the host material. Moreover, the charge-transfer process is one of the basic properties that makes a given transition-metal thiophosphate a suitable cathode material for light-weight solid-state batteries. One or more electrons (up to three) per formula unit may be added to the host-band structure to fill the empty states above the Fermi level. During intercalation, the electronic transfer is influenced not only by the number of empty levels, but also by the band structure itself, i.e., by the density of the electronic states. Thus, there are three possibilities for the transferred electron: it may be in a discrete atomic level, in a molecular level of a discrete polyatomic entity existing in the host structure, or it may be part of a host-lattice conduction band.[1] In this last case, illustrated by the transition-metal dichalcogenides, there is no electronic limitation to the intercalation process and the chemistry is only governed by geometry, i.e., by the number of empty sites in the van der Waals gap. In this way, the intercalation does not shift or change the character of the states near the Fermi level in the energy band of the host. The only change to the host's electronic structure is the increased filling of the conduction band. This approximation is known as the "rigid-band" model and it has been used with success to describe the changes, induced by the lithium intercalation, in the electronic properties of some layered compounds. Since the concept of rigid bands implies the chemical stability of the system, from the energetic point of view, this means that the total energy of the substance is little affected by the addition of intercalant electrons. Thus, the applicability of the rigid-band model may be a test of the most desirable properties of a good intercalation material.[2] The assumption that the

electronic-energy bands of the original crystal are not noticeably affected by intercalation is only reasonable to a first approximation only if the upper valence and lower conduction bands are considered. In fact, the calculations by McCannay for the intercalation complex Li$_x$TiS$_2$ (Ref. 3) have shown that, in this compound, the main modifications are a broadening of the valence s states and a pulling down into the middle of the d manifold of the conduction s states, owing in each case to strong interaction with the Li s state. A much smaller modification to the p and d bands occurs. In the case when the transition-metal–lithium-s conduction band overlaps the filled or partially filled d bands, the attempts to describe the change in the basic electrical properties of the host material, within the framework of the simple charge-transfer–rigid-band model, may be totally erroneous.

Since a clear picture concerning the effect of the lithium intercalation on the transition-metal thiophosphates electrical properties has not been defined, but only some preliminary studies,[4] we have concentrated our attention on this subject, particularly on the nickel thiophosphate compound. In fact, NiPS$_3$ is a host for the lithium intercalation because of its high capacity for the uptaking of lithium. Three lithium ions per molecular unit can be intercalated, two of them reversibly, keeping the electrode potential of the secondary cell at a high value. Moreover, the process of the lithium intercalation is completely reversible and does not cause any lattice expansion of the unit cell. Even if this thiophosphate has been the subject of considerable experimental attention[4-10] and many of its physical properties are now well established, there are various open questions such as the mobility of the lithium ions in the gap, the charge-transfer mechanism, and the nature of the reduction sites, i.e., the NiPS$_3$ low-lying empty levels that accept the lithium 2s electron. In shedding light on these problems, it is necessary to know some details of the electronic structure of both the host system and its intercalation complex.

While the electrical-transport properties of NiPS$_3$ have been studied and satisfactorily interpreted,[8] no systematic study of these properties has been performed yet for

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the lithium chemically intercalated $NiPS_3$. Therefore, we have examined the effects of the lithium intercalation on the electrical-transport properties of $NiPS_3$, interpreting the results on the basis of the so-called transition-metal weakly interacting model.[11] Even if it is well established by means of NMR measurements that the lithium atoms are nearly fully ionized in the intercalated $NiPS_3$ system,[12] the nature of the low-lying empty levels of $NiPS_3$, which accept the Li $2s$ electrons, is not yet fully known. In this regard, all the possible empty levels of $NiPS_3$ have been considered, e.g., the $4s$ and $3d$ orbitals of Ni^{2+} ions, the antibonding orbitals of P-P, bands and the S $3p_z$ orbitals. The main aim of this paper is to identify the conduction mechanism of the involved energy levels of the intercalated sample $Li_x NiPS_3$. In particular, in this paper, we present the in-plane electrical-conductivity measurements as a function of temperature on some systems $Li_x NiPS_3$ intercalated for different times over the temperature range from 185 to 350 K. The intercalation is chemically achieved by means of the n-butyllithium reaction. On varying both the lithium concentration and the temperature, evidence of a new conduction mechanism is found and a possible nature of the reduction sites is proposed. The intercalation time dependence of the intralayer electrical conductivity of the lithium-intercalated $NiPS_3$ is also analyzed and it has been possible to relate these data by means of a simple empirical model.

EXPERIMENTAL PROCEDURES

Chemical lithium intercalation was performed by the classical reaction with n-butyllithium. Single crystals of $NiPS_3$ were immersed for a given time, at room temperature under argon atmosphere, into an excess of a $1.6m$ n-butyllithium solution in n-hexane, where m represents 1 mol/1000 g of solvent. Ohmic contacts were made by soldered pure indium metal on the sample edges before the lithium intercalation. Since the $Li_x NiPS_3$ compounds readily react with moisture, all the preparation was carried out in a glovebox filled with argon gas. Some intercalation complexes $Li_x NiPS_3$ were prepared by transferring each sample (with two indium contacts attached on its edges) from the above bath of n-butyllithium to a large bath of hexane after different periods of time. Thus, each sample was characterized by a given time of immersion in the $1.6m$ n-butyllithium solution in n-hexane and therefore by a different lithium concentration. The effect of the transfer to the hexane bath was to stop further lithium insertion. Time was allowed for an equilibrium distribution of lithium to be attained before measurements were made: at least 24 h under vacuum after the transfer to the hexane bath.

The $Li_x NiPS_3$ samples so obtained were transferred from the dry box to a cryostat, which operates from liquid-N_2 temperature up to about 400 °C. In this cryostat, the temperature dependence of the dc electrical intralayer conductivity of these intercalation compounds was examined using the constant-current two-terminal method over the temperature region from 185 to 350 K. It was not possible to investigate the temperature range above 350 K since the intercalated materials show a non-

reversible decomposition.[4] The Ohmic behavior of the contacts was checked and no evidence of contact resistances was observed. Sample areas were typically between 0.3×0.37 cm^2 and thickness usually varied from 50 to 100 μm. The measurements were repeated at least twice every 24 h. The electrical conductivity of the samples showed no significant change.

The dc electrical conductivity of each single sample was also monitored during intercalation using a constant-current two-terminal method. A microcomputer system was used to control the timing and to collect the data. A low constant current was applied to the sample for a short period, and measurements were taken for a short fixed time so that the intercalation process was practically undisturbed. The Ohmic behavior of the contacts was checked for each measurement. Intercalation starts by the edges of the sample and remarkable Li concentration gradients could establish within it. In order to check the effect of a possible inhomogeneous lithium distribution on these time-dependent measurements, we compared these results with the room-temperature conductivity values of samples in equilibrium (i.e., of those samples used in the above-reported temperature-dependent measurements).

Atomic-absorption measurements of the intercalation complex $Li_x NiPS_3$, corresponding to intercalation times greater than 8000 s, led to a $Li_{1.03}NiPS_3$ formula. This result is consistent with the x-ray photoemission spectroscopy (XPS) analysis of the Li $1s$ and Ni $2p$ peaks, carried out on another $Li_x NiPS_3$ sample intercalated for the same time.

RESULTS

Figure 1 represents the electrical-conductivity variation with the temperature and with the intercalation time in the temperature range from 185 to 350 K for some intercalation complexes $Li_x NiPS_3$. Clearly one observes that the temperature dependence of the conductivity shows an evolution with the intercalation time, i.e., with the lithium content, from an activated behavior to an almost unactivated one. In fact, the unintercalated sample conductivity (curve a) is of about 2×10^{-10} Ω^{-1}cm^{-1} at 300 K and is thermally activated at high temperatures [i.e., σ varies as $\exp(-E_a/kT)$], the activation energy for the electronic conduction being 0.8 eV in accordance with previous measurements.[8] As intercalation time rises, the conductivity increases rapidly, while the activation energy E_a drops from 0.8 eV (curve a) down to 0.01 eV (curve e), showing a substantially temperature-independent conductivity throughout the entire temperature range.

The above variation of the activation energy E_a with the intercalation time is illustrated in Fig. 2. In this figure the experimental data (filled circles) are represented together with the fitting curve (solid line).

Figures 3(a)–3(c) show the electrical-intralayer-conductivity data (open circles) as a function of the lithium intercalation time for three $NiPS_3$ samples placed in contact with butyllithium-hexane solutions of varying concentrations. The different concentrations were ob-
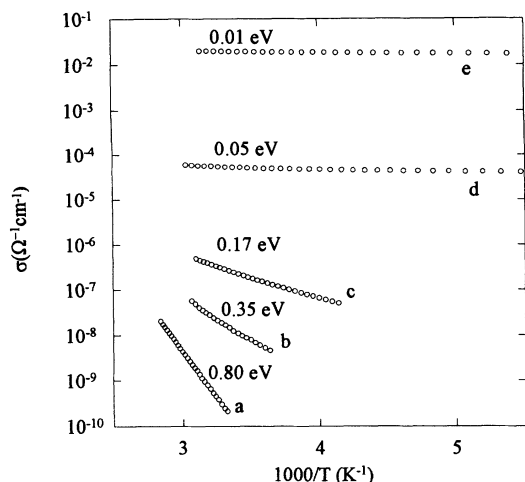
FIG. 1. The electrical intralayer conductivity as a function of temperature and of the lithium-intercalation time for some $Li_x NiPS_3$ crystals. Curve a is attributed to the unintercalated $NiPS_3$ sample, while curves b, c, d, and e refer to intercalation times of about 30, 60, 700, and 8000 s, respectively. The activation energy values E_a are also reported.

tained by changing the strength of the $1.6m$ solution of n-butyllithium dissolved in hexane. This was attained by adding more hexane. Thus, in Fig. 3(a) a single crystal of $NiPS_3$ was left in contact with a 0.5% BuLi-hexane solution, while in Figs. 3(b) and 3(c) with a 3.2% and 9.2% BuLi-hexane solution, respectively. The dashed and solid lines represent, respectively, the free-parameter and the fixed-parameter fitting curves to be discussed in the next section. The full squares shown in the inset of Fig. 3(c) represent the room-temperature data taken from the curves of Fig. 1 multiplied by a constant. It is worth noting that, even if these data refer to samples in equilibrium prepared under similar but not identical conditions, they almost perfectly reproduce the time behavior followed by the open circles, confirming the consistency of the two sets of data. As one can see, the electrical conductivity varies rapidly in the beginning of the intercalation and then proceeds at a considerably lower rate, reaching a
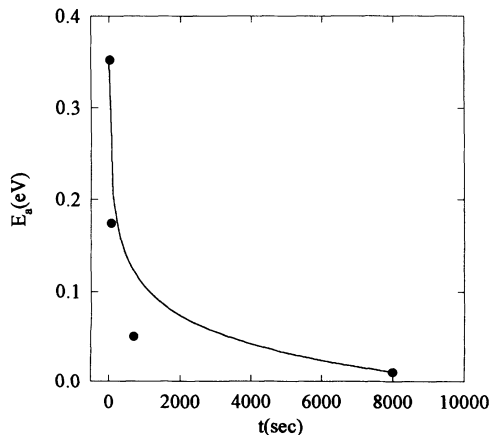

FIG. 2. The variation of the activation energy E_a with the intercalation time. The filled circles represent the experimental data, while the least-squares fit is reported with the solid line.

maximum of about 10^{-1} $\Omega^{-1} cm^{-1}$. This value is achieved in different times for the three samples according to the solution lithium concentration and to the sample thickness. The overall change observed in the $NiPS_3$ electrical conductivity is of about nine orders of magnitude, the unintercalated material-conductivity value being of about 2×10^{-10} $\Omega^{-1} cm^{-1}$. The conductivity data, presented in Fig. 3, do not show a $t^{1/2}$ functional dependence, as expected by the classical diffusion theory in a presumed two-dimensional structure.[13] This different behavior will be discussed in the next section.

Figure 4 shows the log-log plot of the electrical conductivity σ vs the intercalation-time t curves of Fig. 3, referring to the early intercalation times.
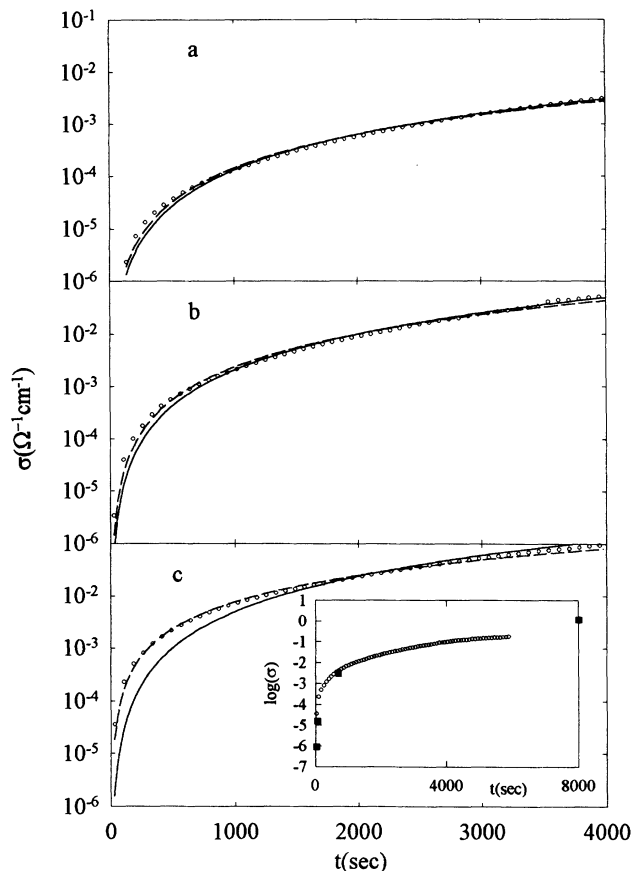
In Table I the parameters values, obtained from a

FIG. 3. (a) The electrical intralayer conductivity as a function of the lithium-intercalation time for a $NiPS_3$ crystal placed in contact with a 0.5% BuLi-hexane solution. The solid line represents the fixed-parameter fit, the dashed line the free-parameter fit, and the open circles the experimental data. (b) The electrical intralayer conductivity as a function of the lithium-intercalation time for a $NiPS_3$ crystal placed in contact with a 3.2% BuLi-hexane solution. The solid line represents the fixed-parameter fit, the dashed line the free-parameter fit, and the open circles the experimental data. (c) The electrical intralayer conductivity as a function of the lithium-intercalation time for $NiPS_3$ crystal placed in contact with a 9.2% BuLi-hexane solution. The solid line represents the fixed-parameter fit, the dashed line the free-parameter fit, and the open circles the experimental data. The full squares, shown in the inset, represent the room-temperature data taken from the curves of Fig. 1 multiplied by a constant.
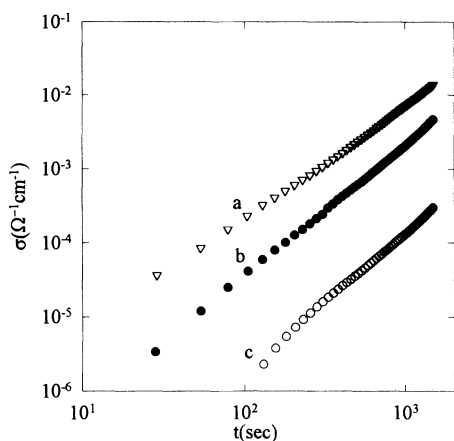
FIG. 4. The electrical intralayer conductivity as a function of the lithium-intercalation time in the early intercalation times for three $NiPS_3$ crystals placed in contact with curve a a 9.2% BuLi-hexane solution, curve b a 3.2% BuLi-hexane solution, and curve c a 0.5% BuLi-hexane solution.

least-squares-fitting procedure applied to the experimental data of Fig. 3, are listed together with the calculated value of the lithium-diffusion coefficient D in the $NiPS_3$ host.

DISCUSSION

As already mentioned in the Introduction, the lithium-intercalated $NiPS_3$ has been the subject of numerous experimental investigations.[1,5,7,10,12,14-17] The lithium atoms are expected to behave as donor intercalants, which transfer $2s$ electrons into the band states of the host lattice. In the van der Waals gap there is one empty octahedral site per formulation $[S\,Ni_{2/3}\,(P_2)_{1/3}\,S]$, i.e., 1.5 site for one $NiPS_3$ unit. Due to a difference in the nature of the second neighbors, octahedral sites fall in two groups: $2d$ and $4h$ sites, respectively, in the Wyckoff notation for this structure with space group $C_{2/m}$. When intercalating, 0.5 lithium occupies completely the first type of sites and further lithium atoms occupy the second type of sites up to $Li_{1.5}NiPS_3$. For the system Li_xNiPS_3, only some room-temperature values for the electrical conductivity as a function of the lithium concentration and some indications about the temperature-dependence type are available in the literature.[4,7,15] This is in part due to the lack of an appropriate theoretical band-structure model for the unintercalated $NiPS_3$ compound and, therefore, for its lithium-intercalated complexes, in

terms of which all the experimental data can be interpreted. Moreover, the electronic model often employed to describe the charge transfer, which accompanies the intercalation process, is the so-called "rigid-band" model, in which it is assumed that the only change to the host-material electronic structure is the increased filling of the conduction band.[18] Therefore, we will adopt this model together with the simplified version of the semiempirical energy-level scheme, deduced from the so-called "transition-metal weakly interacting" model and used to describe the electronic-band structure of $NiPS_3$,[8] as a guide for interpreting our experimental results for intercalated complexes.

As reported in the literature,[19] the diffusion is responsible for the intercalation process. Thus, in order to discuss in detail the conductivity data of the lithium-intercalated $NiPS_3$ it is important to take into account the classical diffusion theory results in a presumed two-dimensional structure.[13,20,21] As intercalation begins, the lithium atoms diffuse from the sample edges exposed to the electrolyte into the bulk. A lithium concentration gradient depending on the time and on the distance from the crystal edges is present: the concentration of lithium atoms at the edges is larger than the concentration corresponding to a uniform distribution of lithium throughout the sample. In the case of the diffusion of lithium into the $NiPS_3$ host, the classical diffusion theory[13,20,21] predicts, for times shorter than s^2/D (D is the coefficient diffusion of the intercalant ions and s is the sample thickness), a $t^{1/2}$ functional dependence for the electrical conductivity σ. This should be true if the electron given up to $NiPS_3$ from lithium during intercalation contributes to the conduction mechanism as a free electron. Indeed, when the host lattice is a semiconductor, one expects the transferred electron to go in a lattice conduction band at least for large enough concentration[22] and thus to be influenced by the conduction mechanism that characterizes the host lattice.

As illustrated in Fig. 1, the electrical conductivity of the intercalated complexes Li_xNiPS_3 obtained for short intercalation times (30 s, curve b and 60 s, curve c, respectively), shows higher values and maintains an activated behavior, the activation energy being 0.35 and 0.17 eV, respectively. Such behavior may be the reason for the departure from the ordinary $t^{1/2}$ law as observed in Fig. 3. In fact, if we hypothesize that at the beginning of the lithium intercalation the electrical conductivity is due to a diffusion process "modulated" by a thermally activated one, the following empirical functional depen-

TABLE I. Parameter values deduced from the fixed-parameter fit and from the free-parameter one. The value of the lithium diffusion coefficient D is also reported.

% n-BuLi in hexane	According to Eq. (3) keeping the n' parameter fixed			According to Eq. (3) leaving all the parameters free			
	σ_0 ($\Omega^{-1}cm^{-1}$)	t_0 (sec)	D (cm^2/sec)	σ_0 ($\Omega^{-1}cm^{-1}$)	t_0 (sec)	n'	D (cm^2/sec)
9.2	2.02×10^{-1}	473.9	9.5×10^{-8}	9.67×10^{-1}	649.9	1.196	6.9×10^{-8}
3.2	9.43×10^{-2}	600.1	3.1×10^{-8}	6.81×10^{-2}	574.5	1.582	3.0×10^{-8}
0.5	8.07×10^{-3}	1100.1	1.8×10^{-8}	6.55×10^{-3}	1088.1	1.643	1.8×10^{-8}

dence can be suggested in the early times of intercalation for σ:

$$\sigma = \sigma_0(t/t_0)^{1/2}\exp(-E_a/kT) ,\qquad (1)$$

where σ_0 is the limiting conductivity at saturation, t_0 is equal to $\pi s^2/16D$, E_a is the activation energy, k is the Boltzmann constant, and T is equal to 300 K. It is worth noting that in Eq. (1) the activation energy E_a is not constant but depends on the intercalation time, and, therefore, on the lithium concentration (see Fig. 2). To choose the correct expression for the activation energy as a function of the intercalation time, we represented the conductivity σ vs the intercalation time t curves shown in Fig. 3 on a log-log plot referring only to the early intercalation times (see Fig. 4). Since, as one can see in Fig. 4, the conductivity has a t^n functional dependence with $n > 1$, we fitted the activation energy E_a vs the intercalation-time t curve, represented in Fig. 2, to a relation of the type

$$E_a = -n \ln(t/t^*) ,\qquad (2)$$

where $t^* = 10\,000$ s was chosen because of normalization purposes. Such a fit is reported as a solid line in Fig. 2; the estimated value of the n parameter is 0.0458. Substituting Eq. (2) for E_a in Eq. (1) we obtain the following expression:

$$\sigma = \sigma_0(t/t_0)^{1/2}(t/t^*)^{n'} ,\qquad (3)$$

where $n' = n/kT$ and T is equal to 300 K. Equation (3) was used to fit the early intercalation times σ vs t curves of Fig. 3. In order to test the quality of this empirical model, we carried out the above fitting procedure either keeping the n parameter fixed to the value obtained from the fit to Eq. (2) or leaving all the parameters free. Thus, in Fig. 3 the fixed-parameter fit is represented by the solid line, while the free-parameter one is reported with dashed lines. It is worth noting that the fixed-parameter fit seems to match quite well with the experimental data, supporting the empirical model expressed by Eq. (3).

According to the classical diffusion theory for times shorter than s^2/D and within the limits of the above-described empirical model, an estimation of the lithium-diffusion coefficient could be given from the relation

$$D = \frac{\pi s^2}{16t_0} ,\qquad (4)$$

where s is the sample thickness. The obtained values, listed in Table I, show a chemical-diffusion coefficient increasing as the butyllithium solution concentration rises. Although these values have to be considered only as indicative, it is worth noting that they agree well with the data reported by Julien et al.,[10] who claim a similar behavior in the $Li_x NiPS_3$ systems for $x < 0.5$.

Going back to Fig. 1, the conductivity of the $NiPS_3$ crystals intercalated for longer times (700 s, curve d and 8000 s, curve e, respectively) does not practically depend on temperature, but its value tends to grow with the lithium content. Therefore, the lithium insertion in $NiPS_3$ produces two main effects on the electrical conductivity of the unintercalated sample: an overall and quick increase in σ and a contemporaneous decrease in the ac-

tivation energy. The observed increment in the electrical conductivity of the $NiPS_3$ lithium intercalates is believed to result from a continuous and quick increase in the carrier concentration due to the transfer of electronic charge from the fully ionized lithium to $NiPS_3$. Such a conductivity increase, together with the intercalation time dependence of the activation energy shown in Fig. 2, suggests the possibility that a new conduction mechanism occurs at a different energy level: namely, a conduction process due to the $2s$ electrons given up to $NiPS_3$ from the intercalated lithium, which overrides the conductivity by holes in the P $3p_z$ valence band suggested for the unintercalated samples $NiPS_3$.[8] Without Seebeck-effect measurements it is not possible to establish the exact nature of the dominant charge carriers; nevertheless, since lithium most likely behaves as a donor specie, the remarkable increase in the electrical conductivity and the intercalation time dependence of the activation energy (see curves d and e in Fig. 1) seem to suggest that this conduction process is by electrons in the extended-band states. Even if it is well established by means of NMR measurements that the lithium atoms are nearly fully ionized in the intercalated $NiPS_3$ system,[12] the nature of the reduction sites, i.e., the low-lying empty levels of $NiPS_3$ that accept the Li $2s$ electrons, is not yet fully known. In this regard, all the possible empty levels of $NiPS_3$ have been considered, e.g., the $4s$ and $3d$ orbitals of Ni^{2+} ions, the antibonding orbitals of P-P bands, and the S $3p_z$ orbitals. From infrared spectroscopy[23] it appears that the P_2 pairs cannot be considered as oxidizing centers, since the ν_{P-P} band remains at constant frequency in the whole investigated intercalation domain of $Li_x NiPS_3$. A possible reason for the exclusion of the Ni $3d$ states as acceptor levels can be formulated as follows. Since in the Ni metal the $3d$ band is only $\frac{1}{15}$ as wide as the $4s$ band,[24] we can expect that in $NiPS_3$, where octahedral sites within each layer are occupied by the Ni^{2+} ions and the P_2 pairs, the increased internuclear distance between the Ni^{2+} ions reduces the $3d$-band width still further on. Since in the transition-metal weakly interacting model[11] the $3d$ electrons are considered to occupy discrete energy levels localized on the nickel cations, they will be characterized by a very low mobility value, which can hardly take into account the overall conductivity behavior. A localization of the electrons given up by the lithium atoms on the nickel $4s$ and sulfur $3s$-$3p$ orbitals was recently suggested by Julien,[25] who carried out IR absorption spectra on some $Li_x NiPS_3$ samples with $x > 0.5$. Recent results by extended x-ray-absorption fine structure[14] show that intercalation is microscopically biphased between the starting compound $NiPS_3$ and a completely reduced phase $Li_x NiPS_3$ according to

$$x\,Li + Ni^{2+}PS_3 \rightarrow \frac{x}{2} Li_x Ni^0 PS_3 + \left(1 - \frac{x}{2}\right) Ni^{2+}PS_3 .$$

$$(5)$$
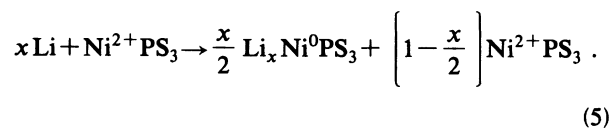
In this expression nickel is reduced at the oxidation-state zero and the reduced nickel atoms move from their initial octahedral sites to tetrahedral ones in the slab. Accord-

ing to Brec,[26] the reduction of Ni^{2+} is a continuous phenomenon starting from $x = 0$ up to 1.5. Therefore, these results seem to favor a localization of the transferred electron on the nickel site. Such a localization was confirmed by our preliminary XPS studies carried out on $Li_x NiPS_3$ intercalates with $x > 1$.[27] In fact, the XPS spectra of the Ni $2p_{1/2}$ and $2p_{3/2}$ peaks for $Li_x NiPS_3$ showed a shift of the main peak towards lower binding energies, thus supporting the nickel-reduction hypothesis. Therefore, in this connection, for the investigated lithium concentrations, the Ni $4s$ states seem to be the possible acceptor levels for the $2s$ electron given by lithium. However, such a hypothesis is valid if both the transition-metal weakly interacting model and the rigid-band one can be adopted for this lithium-intercalated compound. If this condition does not hold, we cannot rule out the possibility that the transition-metal–lithium-s conduction band, derived from the strong interaction between Li s and Ni s states, may be depressed to overlap the partially filled d levels. In such a case it is not possible to exclude that the nickel $3d$ states are the reduction sites together with the Ni $4s$ states.

CONCLUSIONS

The lithiation process induces rather dramatic changes in the $NiPS_3$ electrical-transport properties, which can be summarized as follows: an overall and quick increase in the conductivity value and a contemporaneous decrease in the activation energy. These effects suggest that, with respect to the pure $NiPS_3$, a new conduction mechanism occurs at a different energy level since the very beginning of the intercalation process: a conduction process in the extended-band states due to the $2s$ electrons given up to $NiPS_3$ from the intercalated lithium.

Since the classical diffusion theory is not able to justify the time dependence of the electrical conductivity, a simple empirical model has been formulated, which takes into account the thermally activated nature of the conductivity in the early intercalation times. The behavior of the lithium-diffusion coefficient as a function of the lithium concentration, deduced from this model, is in accordance with that reported in the literature by Julien *et al.* for a lithium content $x < 0.5$.[10]

The reduction of Ni^{2+} to Ni^0, suggested by various experimental results,[1,10,14,16] seems to favor a localization of the lithium $2s$ electron on the nickel site. Since, according to the transition-metal weakly interacting model the nickel $3d$ levels are discrete and localized, the reduction of Ni^{2+} ions suggests that the accepting levels are more likely provided by the Ni $4s$ orbitals.

ACKNOWLEDGMENTS

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