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Preparation and chemical and physical properties of the new layered phases $Li_xTi_{1-y}M_yS_2$ with $M=V$, Cr, or Fe

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We have prepared the layered compounds $LiTi_{1-y}M_yS_2$ ($M=V$, Cr, Fe) by direct synthesis from a mixture of Li_2S and the appropriate elements. The structure of these compounds is $1T$ for $M=V$ and Cr, and $3R$ for $M=Fe$. In the Fe case two phases are obtained for $y>0.66$. Magnetic and Mössbauer data indicate that Fe is divalent and in the high-spin state for $y<0.5$ (effective magnetic moment ~ 4.6 Bohr magnetons), that Cr is trivalent (effective magnetic moment ~ 3.4 Bohr magnetons), and that V is nonmagnetic. The lithium can be removed by reaction with I_2 in an acetonitrile solution at room temperature, producing layered compounds containing oxidized sulfur if $M=Cr$ or Fe. The Cr and Fe compounds are metastable, decomposing above 300 °C into TiS_2 and Cr_2S_3 or FeS_2. In $Ti_{1-y}V_yS_2$ the V is in the 4+ state and has a local magnetic moment at low concentrations. Cr and Fe are trivalent, and the latter is in the low-spin state. Consequently, the valences are assigned as follows: ${Ti^{4+}}_{1-y}{M^{3+}}_y(S^{(2-y/2)-})_2$. In the Cr case the compounds are poor electrical conductors, indicating that the y holes are localized, either by the cation disorder or by forming stable monovalent and divalent sulfur atoms (the monovalent species might form S_2 pairs in this case, but they dissociate when lithium is reintercalated). Since the Fe compounds remain conducting, the holes are not localized and a band picture with the Fermi level moved well into the valence band to produce y holes applies. Electrochemical measurements in nonaqueous lithium cells showed behavior similar to that of TiS_2. Those compounds containing large amounts of Fe could be intercalated with more than one lithium per transition metal, but the reaction beyond $x=1$ was irreversible.

INTRODUCTION

The physical and chemical properties of lithium intercalated into layered transition-metal dichalcogenides have been intensively investigated.[1] In particular, electrochemical reactions with lithium have been studied because of the possible use of such materials in nonaqueous rechargeable batteries. TiS_2 (Ref. 2) and $(V,Fe)S_2$ (Ref. 3) appear to be the best materials in this class for that purpose. In the Li_xTiS_2 system a continuous single-phase intercalation product is found for $x<1$, leading to a continuous but sloping voltage-composition relation in electrochemical cells.[2] At $x=1$ the potential drops sharply to a plateau near 0.5 V, which extends to $x=2$ but is electrochemically irreversible.[4] A recent study of the high-temperature phase of Li_2FeS_2 (Ref. 5) showed that this compound could be cycled electrochemically from $x=0.25$ to 1.8 with the cell voltage remaining near 2 V. However, the reaction was slow, leading to large polarization of the cell at low current drains. Since Li_2FeS_2 was found to have a layered structure, we wished to make alloys with $LiTiS_2$ in hopes of increasing the reaction rate of the Fe compound. Furthermore, it might be expected that the cell potential of Li_xTiS_2 would be increased for $x>1$ as the iron concentration increased. While it is not obvious that such alloy compounds might form, previous work in the system $Li_x(V,Fe)S_2$ suggested that disorder on the transition-metal site would improve the cell capacity and reversibility.[3] These observations lead us to attempt to prepare compounds of the following stoichiometry: $Li_xTi_{1-y}M_yS_2$, where $M=V$, Cr, or Fe.

We have found that these compounds can be prepared for $0<x<1$ and for $0<y<1$ except for Fe, where $y<0.66$. A further exception is that Li cannot be removed from $LiCrS_2$ (or $LiTi_{1-y}Cr_yS_2$ for $y>0.75$). Here we report the structure of such compounds, and show that the sulfur is oxidized in some of these compounds, leading to unusual valence states of the sulfur. Measurements of the magnetic susceptibility and Mössbauer spectra (for Fe) aid in determining the valence states of each atomic species. The electrochemical behavior of these new cathode materials is also reported and discussed.

PREPARATION AND STRUCTURE

Appropriate amounts of Li_2S, S, and MS ($M=Ti$, V, Cr, or Fe) were mixed together under an inert atmosphere and placed in a graphite boat. The boat was sealed in quartz and the sample was heated slowly over several days to 600—900 °C, the latter temperature being required to obtain a homogeneous product for $M=V$ or Cr. After three days at constant temperature the samples were removed to a helium dry box, where they were opened and thoroughly ground. Then they were refired at 600—750 °C for several more days. Since these compounds are mois-

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ture sensitive, they were always handled in a helium atmosphere.

Lithium was removed to form $Ti_{1-y}M_yS_2$ by treatment with iodine in acetonitrile as previously described.[3] When $M = $ Cr, complete removal of the Li was possible only for $y \leq 0.75$. This reaction is quantitative and confirmed that the starting compounds contain one Li per transition metal (Ti plus *M*) to within the accuracy of measurement (3%): An upper limit on the amount of Li remaining intercalated in the material was obtained by atomic absorption analysis. This produces an upper limit, because the absorption measures *all* the lithium in the sample, including any trapped Li in the form of LiI from the iodine reaction (although the sample is well washed with acetonitrile before such measurements). Such a measurement also gives an upper limit to the amount of Li that could substitute for Ti or *M* within the layers. Absorption measurements of $Ti_{1-y}Fe_yS_2$ found that $x = 0.030, 0.010, 0.032$ at $y = 0.01, 0.05, 0.10$, respectively, after reaction with excess iodine in acetonitrile. These delithiated compounds are metastable. Above 250—300 °C the compounds decompose irreversibly to form FeS_2 and TiS_2. Relithiation of these samples has also been carried out at room temperature by reaction with *n*-butylLi. However, when using *n*-butylLi overreduction occurs at large *y*. For example, the nominal formulas of Fe compounds relithiated using *n*-butylLi are as follows: $Li_{1.03}Ti_{0.9}Fe_{0.1}S_2$, $Li_{1.18}Ti_{0.75}Fe_{0.25}S_2$, and $Li_{2.9}Ti_{0.33}Fe_{0.66}S_2$. The first compound is stoichiometric within our measurement accuracy, while the last compound has decomposed, in that the x-ray diffraction pattern is featureless (characteristic of an amorphous product).

X-ray powder diffraction patterns at room temperature were obtained with the use of a holder, which can be evacuated. In all cases these patterns can be completely indexed on the basis of a hexagonal cell. Figure 1 shows the hexagonal lattice parameters for $LiTi_{1-y}M_yS_2$ ($M = $ V, Cr, Fe) as a function of composition (y). As expected, when $M = $ V or Cr a complete solid solution exists over the whole composition range. In $LiTi_{1-y}Fe_yS_2$ a hexagonal layered structure exists for $y < 0.66$. A two-phase region extends from $y = 0.66$ to $y = 1.0$ so that $LiFeS_2$ is formed as a second phase in this region. At $y = 0.66$ the x-ray lines are broad indicating very small crystallite sizes or short crystalline coherence lengths of about 400 Å. Figure 2 gives the hexagonal lattice parameters for $Ti_{1-y}M_yS_2$ and Fig. 3 shows how the lattice parameters vary with lithium concentration when $M = $ Fe. The lithiated Fe compounds have the 3*R* structure; that is, there are three layers per unit cell stacked so that the 10*l* reflections are absent for $l = 3n$. At $y < 0.1$ the samples also contained some 1*T* polytype (one layer per unit cell). The fraction of the observed 1*T* polytype increased as *y* is decreased. Also the fraction of 1*T* polytype obtained increased upon annealing at high temperatures (700 °C and above). However, it was not possible to produce completely pure 1*T* phase by this high-temperature preparative technique. There is no evidence for a superstructure due to an ordering of *M* and Ti; however, such ordering would produce very weak superlattice reflections, since the x-ray scattering powers of *M* and Ti are so similar, so that such reflections might be too weak to observe with the usual diffraction techniques. Relithiation of $Ti_{1-y}M_yS_2$ using *n*-butylLi or an electrochemical cell produces products having the 1*T* structure only, even if the initial compound had the 3*R* structure. The unit-cell volume versus composition is shown in Fig. 4 (if the structure is the 3*R* polytype, then one-third of the unit-cell volume is given).

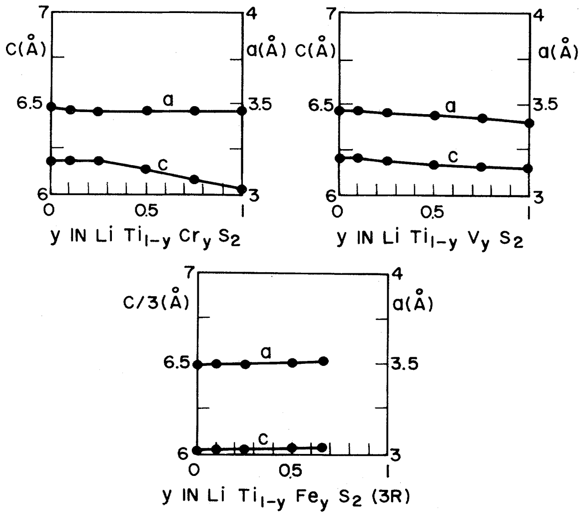

FIG. 1. Hexagonal lattice parameters of $LiTi_{1-y}M_yS_2$ are given as a function of concentration y. When $M = $ V or Cr, a complete solid solution exists between the end points and the structure type is 1*T*. For Fe a solid solution exists for $y < 0.66$ but the layered structure type is 3*R*. Consequently, the *c* axis is divided by 3 to allow a direct comparison with the other two cases.

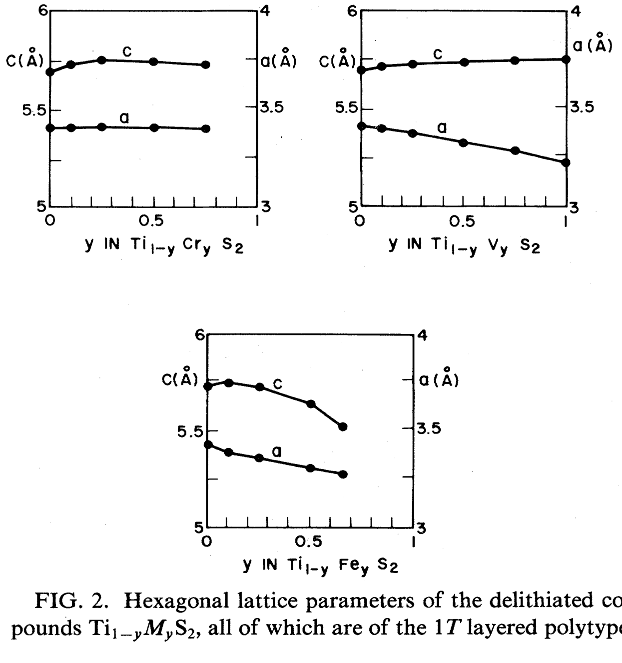

FIG. 2. Hexagonal lattice parameters of the delithiated compounds $Ti_{1-y}M_yS_2$, all of which are of the 1*T* layered polytype.

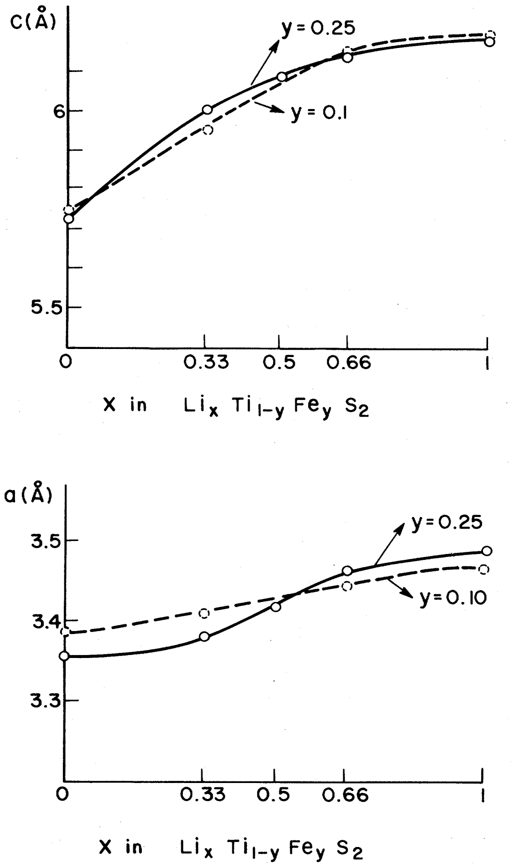

FIG. 3. Variation of the lattice parameters in $Li_xTi_{1-y}Fe_yS_2$ at $y = 0.10$ and 0.25 is shown vs the lithium concentration x.

PHYSICAL AND ELECTROCHEMICAL PROPERTIES

In this section we report the results of magnetic susceptibility measurements, electrical resistivity measurements (on pressed powders), Fe Mössbauer spectra, and electrochemical studies. The magnetic susceptibility was measured by the Faraday method from 4.2 to 350 K on most of the samples prepared. The lithiated samples are air sensitive, so they were loaded into quartz tubes in the glove box and sealed under a helium atmosphere. In all cases the susceptibility increased in a Curie-type manner upon cooling the sample as seen in Figs. 5—7. The data were least-squares fitted to the Curie-Weiss form $\chi_g = C_g/(T+\Theta)+\chi_0$ as previously described.[6] Tables I and II show the results of such a fit, along with the temperature interval over which the fit was made and the magnetic moment of the substituted element M (assuming that all atoms M have the same moment). The susceptibility of $LiTiS_2$ is weakly paramagnetic and temperature independent and, at low concentrations of M at least, it is clear that the moments reside on the M atoms.

Room-temperature Mössbauer absorption spectra were obtained on Fe-containing compounds in order to gain further information on the valence and spin state of the

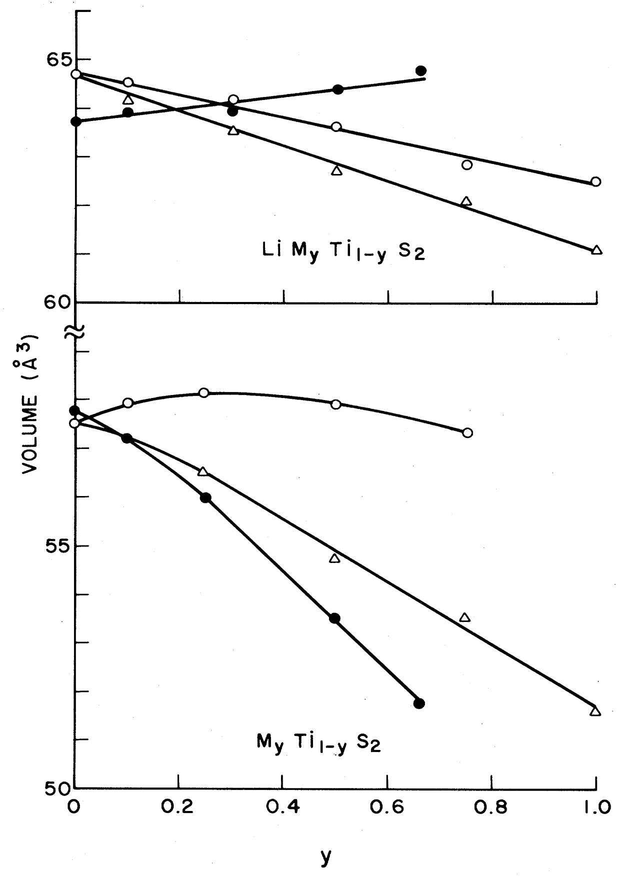

FIG. 4. Volume of the unit cells of all the compounds is shown vs the concentration of M. The volume of $LiTi_{1-y}Fe_yS_2$ is divided by 3 since the unit cell is the 3R polytype and includes three layers (triangles, $M=V$; open circles, $M=Cr$; closed circles, $M=Fe$).

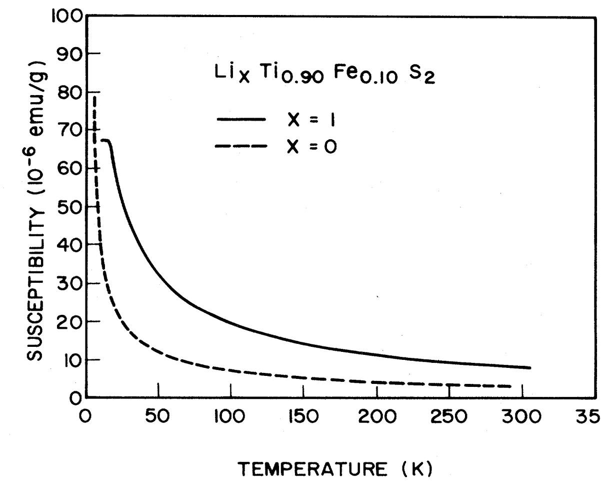

FIG. 5. Magnetic susceptibility of an Fe-containing compound at $x = 1.0$ and 0.0 is shown from 4.2 to 300 K.

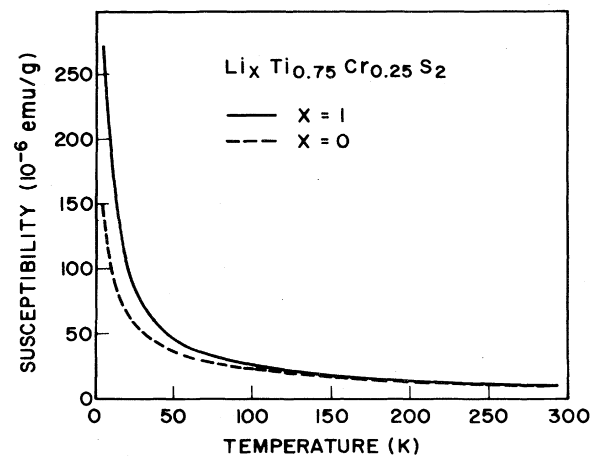

FIG. 6. Magnetic susceptibility of $Li_xTi_{0.75}Cr_{0.25}S_2$ for $x = 0.0$ and 1.0 is given from 4.2 to 300 K.

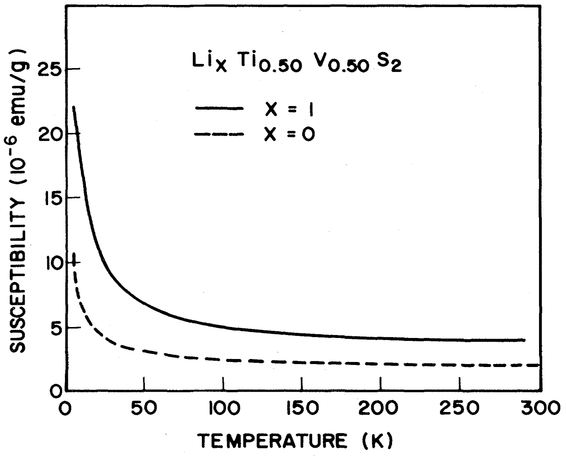

FIG. 7. Magnetic susceptibility of vanadium-substituted compounds shows a small increase at low temperatures.

Fe. Spectra for these compounds are shown in Figs. 8 and 9. The gamma-ray source is ^{57}Co in Pd metal. These spectra differ from those seen in well-ordered Fe-containing compounds. In the present compounds the Mössbauer lines are broad for $y > 0.05$, reflecting the local disorder inherent in substitutional alloys. At large y more than two lines are clearly seen, indicating different local atomic arrangements about the Fe (Fig. 8). Spectra of samples at $y = 0.25$ as a function of lithium concentration are shown in Fig. 9. The center shift increases rapidly near $x = 0.5$ upon increasing x (Fig. 10), and in this same region the quadrupole splitting increases as well (Fig. 11).

TABLE I. Parameters obtained from a fit to the Curie-Weiss law are given for the compounds $Li_xTi_{1-y}M_yS_2$. Shown are the Weiss constant Θ, the temperature-independent susceptibility, the effective magnetic moment per M atom derived from the Curie constant C, the temperature interval over which the fit was determined, and the rms deviation of the data from the Curie-Weiss law (in percent).

Compounds $Li_xTi_{1-y}MS_2$		Θ (K)	χ_0 (10^{-6} emu/g)	Magnetic moment (μ_B)	Interval (K)	σ (%)
$x = 1$						
M=Fe	$y = 0.01$	3	1.24	4.56	10–300	0.47
	$y = 0.05$	12	1.24	4.47	25–300	0.34
	$y = 0.10$	18	1.23	4.53	25–300	0.30
	$y = 0.25$	48	0.59	4.80	50–300	0.15
	$y = 0.50$	90	1.75	4.79	100–350	0.24
M=Cr	$y = 0.1$	6	1.40	3.40	30–300	0.64
	$y = 0.25$	6	1.88	3.10	30–300	0.39
	$y = 0.50$	31	3.54	3.03	50–300	0.38
	$y = 0.50$	57	1.09	3.34	100–700	0.22
M=V	$y = 0.1$	10	1.97	1.05	30–300	0.17
	$y = 0.5$	0.7	1.03	0.5	4–50	0.31
$x = 0$						
M=Fe	$y = 0.01$	0.4	0.29	1.91	4–50	0.70
	$y = 0.05$	0.6	3.99	1.39	4–50	0.83
	$y = 0.10$	15	0.59	2.60	30–300	0.31
	$y = 0.25$	38	0.92	2.75	50–360	0.73
	$y = 0.50$	30	6.16	1.42	50–300	0.37
M=Cr	$y = 0.10$	30	0.29	3.54	50–370	0.38
	$y = 0.25$	22	2.41	3.03	50–300	0.56
	$y = 0.50$	26	5.33	2.80	50–300	0.23
	$y = 0.75$	13	9.36	2.25	50–300	0.51
M=V	$y = 0.1$	12	0.24	1.77	30–300	0.27
	$y = 0.25$	14	1.06	1.09	30–300	0.22
	$y = 0.50$	0.5	0.96	0.35	4–50	0.37

TABLE II. Parameters obtained from a fit of the magnetic susceptibility to the Curie-Weiss law in $Li_xTi_{0.9}Fe_{0.1}S_2$.

	C_g (10^{-6} emu/g)	Θ (K)	χ_0 (10^{-6} emu/g)	Magnetic moment (μ_B)	Interval (K)	σ (%)
$Ti_{0.90}Fe_{0.10}S_2$	750	15.0	0.50	2.60	30–300	0.31
$Li_{0.10}Ti_{0.90}Fe_{0.10}S_2$	381	3.0	0.74	1.85	10–100	0.22
$Li_{0.20}Ti_{0.90}Fe_{0.10}S_2$	267	1.8	0.49	1.56	4–100	0.57
$Li_{0.40}Ti_{0.90}Fe_{0.10}S_2$	639	5.5	1.74	2.42	10–130	0.38
$Li_{0.60}Ti_{0.90}Fe_{0.10}S_2$	2015	18.0	1.25	4.405	30–300	0.21
$LiTi_{0.90}Fe_{0.1}S_2$	2139	18	1.23	4.53	25–300	0.30

The Mössbauer data are summarized in Table III, where the center shift and approximate linewidth are given. The width is that measured at half maximum, but the lines are not Lorentzian for $y > 0.05$, as can be seen in Figs. 8 and 9.

As a rough measure of the electrical resistivity, the resistance of a small pellet of each compound was obtained in a homemade press. The approximate dimensions of the pellet were 4 mm in diameter by 6 mm long. A resolution of 0.1 Ω was obtainable with device. All the compounds with $M=V$ or Fe gave resistances of 0.1 Ω or less, indicating resistivities of less than 0.02 Ω cm (including the particle-particle contact resistance). The resistance of such pellets of $LiTi_{1-y}Cr_yS_2$ remained low for $y<0.25$ but increased to 1.5 Ω at $y=0.5$ and was insulating at $y=1$ ($LiCrS_2$). When Li is removed from the Cr compounds, resistances of 10–200 Ω were obtained, indicating semiconducting or localized carrier behavior.

Finally, the electrochemical characteristics were deter-

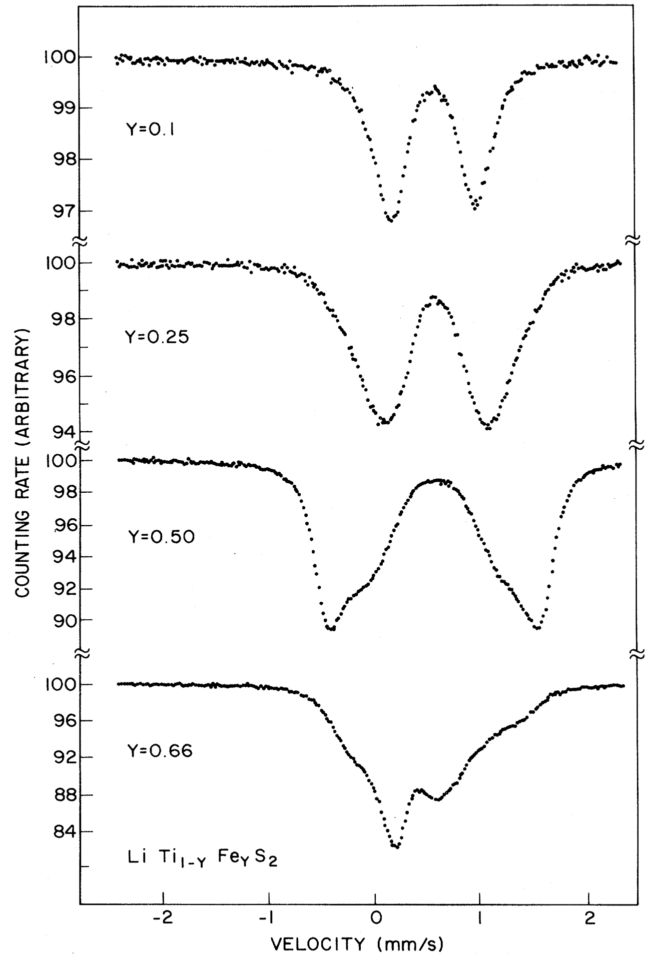

FIG. 8. Room-temperature Mössbauer absorption spectra of $LiTi_{1-y}Fe_yS_2$ are shown as a function of composition.

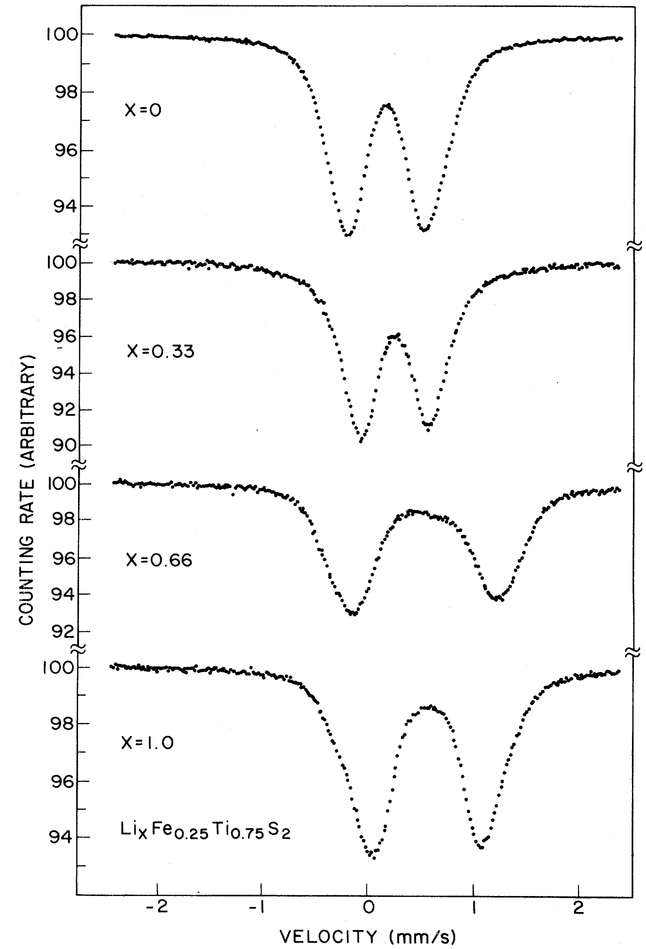

FIG. 9. Room-temperature Mössbauer absorption spectra for $Li_xTi_{0.75}Fe_{0.25}S_2$ for $x=0$ to 1.

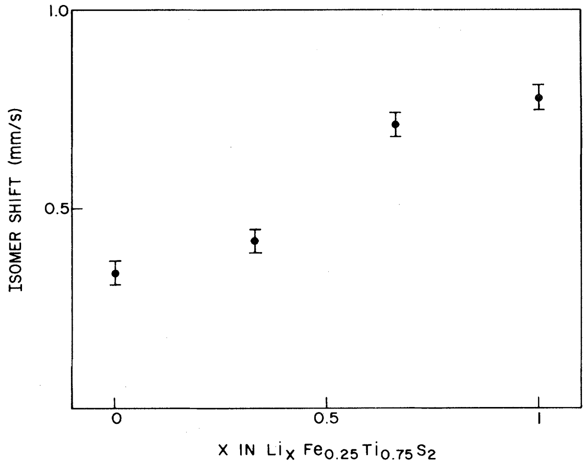

FIG. 10. Center shift with respect to Fe metal vs lithium concentration (x) in $Li_xTi_{0.75}Fe_{0.25}S_2$. The large uncertainty in the center shift indicated by the bars is estimated and due to the non-Lorentzian line shapes.

mined in a cell with a lithium anode and a propylene carbonate-lithium perchlorate electrolyte. The cell design and use was described previously.[3] Typical cell cycling curves are shown in Fig. 12.

DISCUSSION

The properties of these compounds are determined by the electronic state of each element in the material. In chemical terms this means determining the valence and spin state of each element and the nature of the bonding. Equivalently, the properties are determined by the nature of the wave functions at the Fermi level (their atomic character) and the proximity to Mott or Anderson localization. The following discussion addresses these questions.

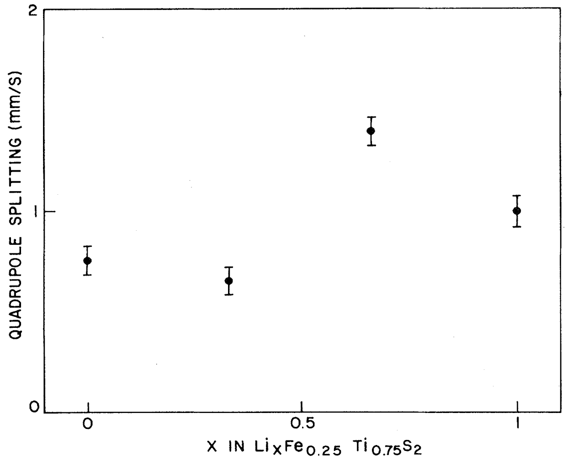

FIG. 11. Room-temperature quadrupole splitting in $Li_xTi_{0.75}Fe_{0.25}S_2$ for $x=0$ to 1.

TABLE III. Approximate values for the center shift (with respect to Fe metal) and linewidths of the Fe^{57} Mössbauer spectra are given for the compounds $Li_xTi_{1-y}Fe_yS_2$. For $y>0.05$, the lines are broader than expected and it is clear that at least two sites with different quadrupole splitting but the same center shift are present, since fits to such spectra with only two Lorentzians are poor. Asterisk entries are given when multiple sites are clearly resolved as multiple maxima (see Fig. 8).

X	Y	CS (mm/s)	Width (mm/s)
0	0.05	0.36	0.33
0	0.10	0.36	0.42
0	0.25	0.33	0.43
0	0.50	0.30	0.38
0	0.66	0.32	0.5
1	0.05	0.78	0.26
1	0.10	0.79	0.39
1	0.25	0.78	0.52
1	0.50	0.77	*
1	0.66	*	*

TiS_2 is a small band gap semiconductor, with a resistivity on the order of $10^{-3}\,\Omega\,cm$.[7,8] When Li is intercalated, it becomes a Li ion,[9] giving its valence electron to the previously empty Ti d band (the Ti is reduced from 4+ to 3+ at full intercalation, $x=1$). When the Ti is replaced by another element, it might be expected that the rules for determining possible substitution would be the same as in other transition-metal compounds, such as oxides or

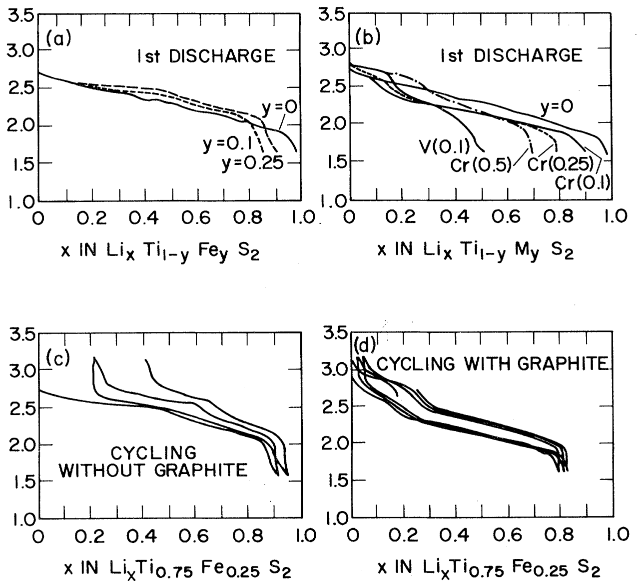

FIG. 12. Potential of cells with a lithium anode and a cathode of the indicated sulfide decreases as the lithium content of the compound increases. The cycling behavior is improved if some graphite is added to the cathode to increase its overall conductivity.

fluorides. That is, substitution would be possible only when the sum of the products of the metal concentration and their valence remains constant. For example, in $Ti_{1-y}M_yS_2$ the rule would give $(1-y)\bar{V}(Ti)+y\bar{V}(M)=4$, where $\bar{V}(Ti)$ is the average valence of the Ti, etc. Since the maximum valence of Ti is 4+, M would need to have a valence of 4+ or greater to satisfy the above rule. This rule obviously comes from the assumption that the anion valence does not change when M is substituted for Ti. Such a rule is always obeyed for oxides and fluorides, but as we shall see is not always valid for sulfides. In these compounds the only valence that can be assumed constant is that of the Li (1+). Because Li is so electropositive, Li is essentially fully ionized in ternary sulfides such as $LiTiS_2$, $LiCrS_2$, or $LiFeS_2$.

First we discuss the fully lithiated compounds, considering Fe, Cr, and V in turn. The lattice constants and unit-cell volumes of $LiTi_{1-y}Fe_yS_2$ are linear in composition, as is usually found for alloy substitutions. The $3R$ polytype of $LiTi_{1-y}Fe_yS_2$ that is obtained from the high-temperature preparation has a smaller unit-cell volume than the $1T$ polytype formed by room-temperature relithiation of $Ti_{1-y}Fe_yS_2$. The smaller volume of the $3R$ polytype is due to the decreased repulsion between the Li^+ and the transition metal in the $3R$ polytype as compared to the $1T$ polytype. Figure 13 shows that the Li and transition-metal atoms sit directly over one another along the c axis in the $1T$ polytype, while the Li is displaced to the side in the $3R$ polytype. The decreased Coulombic repulsion in the latter case leads to a smaller c axis and unit-cell volume. All the cell parameters and volumes shown for $LiTi_{1-y}Fe_yS_2$ in Figs. 1 and 4 are for the $3R$ polytype.

The magnetic data for $y<0.5$ show that the Fe has a magnetic moment of about $4.6\mu_B$. For Fe concentrations larger than 5% the Mössbauer lines are broad and consist of at least two different contributions with very different quadrupole splitting but similar center shift. A center shift of approximately 0.78 mm/sec is found independent of Fe concentration. Both the magnetic moment and the shift are consistent with the Fe being divalent and high spin (the six d electrons on the Fe are localized and have a total spin of 2).[11] Consequently, the valence can be assigned as follows: $Li^{1+}Ti^{4+}{}_yTi^{3+}{}_{1-2y}Fe^{2+}{}_yS^{2-}{}_2$. Since the compounds are conducting, the d electrons on the Ti^{3+} are delocalized into a conduction band. At $y=0.5$ all the Ti is 4+, and the conduction band is empty. The Mössbauer spectrum at $y=0.5$ shows two prominent lines that can be fit with Lorentzian profiles with linewidths of 0.32 and 0.48 mm/sec for the outer and inner pair of lines, respectively. The former linewidth is typical of those obtained in ordered Fe intercalation compounds.[10] The narrowness of the outer lines and only a moderate broadening of the inner lines suggests that the Fe is not randomly distributed at this Fe concentration. However, it is not clear whether this reflects true long-range order of the Fe and Ti or only significant short-range correlations. The two Fe sites are characterized by the same center shift but very different quadrupole splittings. The larger splitting is about 2.0 mm/sec, indicating a very large distortion from cubic symmetry. For $y=0.66$ the Mössbauer spectrum is complex and shows a new pair of lines with a center shift of about 0.6 mm/sec. This value is at the low end of center shifts measured for high-spin Fe^{2+} and at the upper end of those measured for high-spin Fe^{3+}.[10,11] In order for the valences to balance, some of the Fe must be trivalent or the sulfur must be oxidized. This new Fe site seen at $y=0.66$ cannot be due to intercalated Fe, since the lithium is easily removed from and inserted into the compound. Intercalated Fe would pin the layers together and drastically reduce the lithium diffusion rate. Since there are many ternary iron sulfides containing trivalent iron (such as $KFeS_2$), it seems likely that some of the Fe is indeed trivalent. However, since the Mössbauer spectra are so complex and since the possibility of two different Fe magnetic moments with large exchange interactions make the magnetic data similarly difficult to interpret, we cannot be certain of the valence assignments when $y>0.5$.

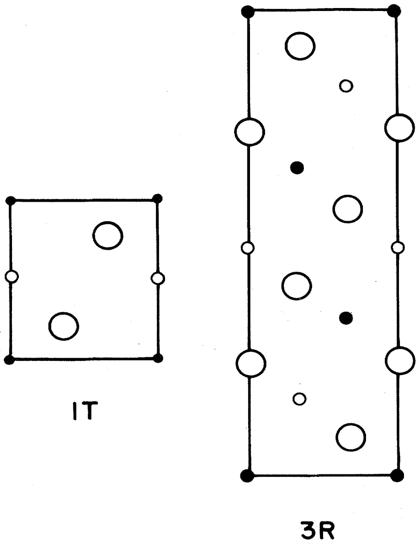

FIG. 13. Unit cell of the $1T$ and $3R$ polytypes contain one and three layers, respectively. The (1120) planes are shown, with the sulfur indicated by the large circles, the titanium (or transition metal) by the solid circles, and the lithium by the small open circles.

The magnetic data in the case of Cr substitution suggest that the Cr is trivalent and high spin ($S=\frac{3}{2}$), as it is in $LiCrS_2$.[12] The fit to the Curie-Weiss law given in Table II shows that the moment obtained decreases as y increases. The true moment per Cr is expected to be larger than this value, since some of the Cr atoms will be antiferromagnetically coupled at temperatures of 100—200 K (the Weiss constant of $LiCrS_2$ is 270 K). In this case the calculated moment is less than the true moment per Cr, and the value of χ_0 increases. This is further reflected in the increase in the moment obtained when the temperature interval of the fit moves to higher temperatures (see Table II for an example at $y=0.5$). It is clear from the value at small y and the trend seen as a function of fitting interval at $y=0.5$ that the Cr has a moment close to that expected for a Cr^{3+} high-spin ion (3.87 μ_B). The valence is then assigned as follows: $Li^{1+}Cr^{3+}{}_yTi^{3+}{}_{1-y}S^{2-}{}_2$.

The last case of the fully lithiated compounds is that of V substitution. In this case the measured magnetic moments are small. As in $LiVS_2$ there are likely a small number of V atoms in antisite positions.[13] These atoms are in the interlayer region displacing an equivalent amount of lithium. Such V is probably trivalent as in V_5S_8.[14] The measured moment could be accounted for by about 2% of the Li being replaced by V; that is, about 20% of the V at $y=0.1$ would need to be in antisite defects. (V^{3+} has a magnetic moment of $2.8\mu_B$.) However, this number of defects seems very high when compared to those present in $LiVS_2$,[13] for example. At high temperatures (greater than 315 K), $LiVS_2$ is highly paramagnetic, suggesting that the V *d* electrons are on the verge of localizing. It seems possible that at low *V* concentrations in $LiTi_{1-y}V_yS_2$ the *intralayer* V will develop a local moment due to decreased overlap with the near-neighbor Ti atoms. However, without a detailed study of the antisite defect density, we cannot be certain of this. In any case, the valences can all be balanced assuming again that the sulfur valence is 2−.

Now we consider the delithiated compounds ($x=0$) containing V, Cr, and then Fe. The magnetic susceptibility of $Ti_{1-y}V_yS_2$ compounds shows a Curie-type increase at low temperatures, similar to that seen in $LiTi_{1-y}V_yS_2$. However, the Curie contribution at low V concentrations is about 3 times larger than in the lithiated ($x=1$) compound. The moment on the V at low concentrations is about $1.8\mu_B$. Again, although we expect a small number of antisite V defects which are paramagnetic, it seems likely that the Curie tail is largely due to paramagnetic *intralayer* V. The moment measured is consistent with one localized electron on V^{4+}. The unit-cell volume decreases by about 6 Å^3 on going from TiS_2 to VS_2. A somewhat smaller decrease (3.7 Å^3) is also seen in the fully lithiated compounds (see Fig. 4). These decreases are expected, since the size of V is smaller than that of Ti (in the same valence state and bonding environment).

When Cr is substituted for Ti in TiS_2, the magnetic moment obtained at low Cr concentrations approaches that expected for Cr^{3+}. At higher Cr concentrations some of the Cr moments become antiferromagnetically coupled at temperatures of at least of few hundred degrees. As in the lithiated compound, this causes the apparent moment and the Weiss constant obtained from a fit to the Curie-Weiss law in the temperature intervals used here to be smaller at higher concentrations than expected for Cr^{3+} and the temperature-independent term χ_0 to increase sharply as seen in Table I. Since the Cr is trivalent, the valences cannot be balanced, assuming that the sulfur remains divalent. We conclude that the sulfur is oxidized in the Cr containing compounds when the Li is removed. The valences are assigned as follows: $Cr^{3+}{}_yTi^{4+}{}_{1-y}(S^{(2-y/2)-})_2$. In a band picture, $y/2$ holes per sulfur are produced in the sulfur valence band. An alternative possibility is that the sulfur atoms become inequivalent: some are divalent and some are monovalent. We will discuss the sulfur oxidation further after discussing the Fe compounds. While the unit-cell volume of $LiTi_{1-y}Cr_yS_2$ compounds varies linearly between the two end points as expected, the unit-cell volume of the delithiated compounds $Ti_{1-y}Cr_yS_2$ varies nonlinearly with *y*. Instead of the cell volume decreasing with increasing *y* as expected, the volume *increases* for $y<0.25$. This is most likely due to the localization of the conduction electrons (holes). Any metal-insulator "transition" usually causes a substantial increase in unit cell volume.

The last delithiated compound to consider is $Ti_{1-y}Fe_yS_2$. The magnetic data show that the *average* moment per Fe is small—about $2.0\mu_B$. At low Fe concentrations ($y<0.05$) the susceptibility could not be fit to a simple Curie-Weiss form over the full temperature range (10—350 K, Table I). In these compounds, the susceptibility increases slightly upon *increasing* the temperature above 200 K. This may be due to a temperature-dependent χ_0 or to a temperature-dependent moment on the Fe due to the thermal population of excited crystal field states. Shown are the results of a best fit at low temperatures only. At $y=0.05$ the values of χ_0 and magnetic moment do not fit in with the trend or with values expected (for χ_0) from the Cr or V case. The data is included here only to show that it is impossible to fit the susceptibility with large Fe moments. Since at $y=0.05$ the Mössbauer lines are narrow, and only slightly broadened at $y=0.10$, we conclude that all the Fe is in the same valence state (all have the same center shift) even though there is a distribution of quadrupole splittings for $y>0.05$. That is, it is not possible that a significant fraction of the Fe has a large moment while the rest has no moment, since the amount of high-spin Fe^{2+} necessary to explain the low moments observed here would have been easily seen in the Mössbauer measurements. The magnetic moments are considerably smaller than that obtained for high-spin Fe^{2+} ($\sim 4.6\mu_B$) or for high-spin Fe^{3+} ($\sim 5.8\mu_B$). The possibility of producing Fe^{4+} seems unlikely, since the only Fe^{4+} compounds known are ternary compounds containing more electronegative anions than sulfur (such as oxygen or fluorine) and another cation that is very electropositive (such as an alkali metal).[15] In any case, the possibility of high-spin Fe^{4+} can be eliminated because its magnetic moment is too large (about $4.8\mu_B$) and low-spin Fe^{4+} can similarly be eliminated on the basis of its expected isomer shift. The center shift of Fe^{4+} (low spin) in oxide compounds is about 0.05 mm/sec.[16] In sulfides center shifts for this state would be expected to be less than or at best equal to this value. The possibility of low-spin Fe^{2+} can also be eliminated since it has no magnetic moment. The moments obtained and the center shift are, however, in the range of those expected for low-spin Fe^{3+}.

We propose a simple electronic model that fits all the data, as follows. In pure TiS_2 the valence band has predominantly S 3*p* character, and the wave functions at the top of the valence band are made up of the nonbonding lone pair orbitals that extend into the van der Waal's gap. The conduction band minimum is about 0.3 eV above the valence band and has predominantly Ti 3*d* character.[17] When Fe substitutes for Ti, the *d* bandwidth decreases due to the reduced overlap of the Ti and Fe *d* functions (since the atomic *d* orbitals are at different energies) and due to the decrease in the number of Ti near neighbors about an individual Ti atom. An energy diagram is given in Fig. 14. When Li is intercalated in TiS_2 the Fermi level is moved well into the *d* band.[18] As Fe is substituted for Ti, the Fermi level falls in order to compensate for the divalent or trivalent Fe. We assume the Fe levels to be essentially localized and independent of concentration. In $LiFe_{0.5}Ti_{0.5}S_2$ the Ti *d* band is empty, since the magnetic and Mössbauer results show that Fe is still divalent and consequently that the Ti is all 4+. This means that the Fe *d* levels must be below the bottom of the Ti *d* band at $y=0.5$ (the dashed line of Fig. 14 shows the bottom of the Ti *d* band in this situation). Since the divalent Fe level lies above the sulfur valence band maximum, the Fe will be oxidized before the sulfur when the Li is removed from $LiFe_yTi_{1-y}S_2$ to produce $Fe_yTi_{1-y}S_2$. The center shift of the Fe at $x=0$ (no Li) is approximately independent of the Fe concentration (0.35 mm/sec), so that the valence at $x=0$ is independent of Fe concentration. This isomer shift is in the range expected for trivalent iron.[19] The trivalent Fe level lies well below the valence band maximum.

We can estimate the energies of the divalent and trivalent Fe states in the following way. If the Fe becomes trivalent upon removal of lithium, electron counting would produce the following valences: $Fe^{3+}{}_yTi^{4+}{}_{1-y}(S^{(2-y/2)-})_2$; that is, there are *y* holes in the valence band. The iron will be reduced from Fe^{3+} to Fe^{2+} when sufficient Li has been added to fill the *y* holes in the sulfur valence band and the portion of the Ti *d* band below the Fe^{2+} level. This latter contribution decreases with increasing *y* so that by $y=0.5$ this contribution is zero. At $y=0.1$ the data in Table II show that the critical concentration of Li to reduce the Fe is $x\sim0.5$. At this Li concentration there are 0.4 electrons per Ti in the *d* band. From band calculations this puts the Fe^{2+} level approximately 0.5 eV above the bottom of the Ti *d* band. Since the *d* band width depends upon the Fe concentration, a better reference point is the top of the valence band. Using a linear approximation for the *d* band width, the fact that the bottom of the *d* band is above the Fe^{2+} level at $y=0.5$, and a *p*-*d* gap of 0.3 eV in pure TiS_2, we find that the Fe^{2+} levels are approximately 0.9 eV above the top of the valence band. The minimum separation between the valence band maximum and the Fe^{3+} level can also be crudely estimated. Since the center shift at $x=0$ (no Li) remains near 0.33 mm/sec for all $y<0.66$, the valence of the Fe remains trivalent even at $y=0.66$. At this Fe concentration there are 0.66 holes in the valence band. A crude estimate of the density of states in the valence band is obtained by dividing the number of states per atom by the band width (12 electrons/5 eV wide). Assuming a constant density of states (rather crude, especially near the band edge), the Fermi level at $y=0.66$ is at least 0.3 eV below the top of the valence band. The Fe^{3+} level must lie below this. This placement of the Fe^{2+} and Fe^{3+} levels is consistent with a recent electronic model of many different iron containing sulfides.[19]

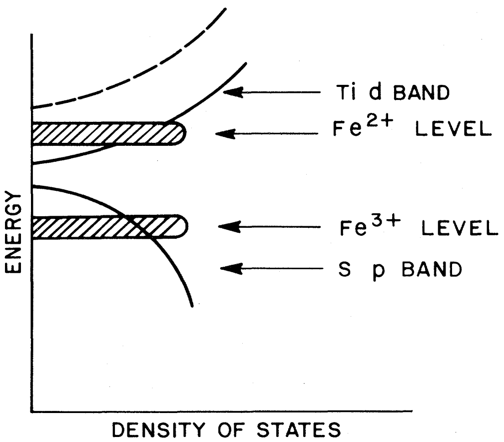

FIG. 14. Electron energy level (band) diagram for $Li_xTi_{1-y}Fe_yS_2$ in the vicinity of the Fermi level. The dashed line indicates that the Ti *d* band is expected to become narrower upon alloying with Fe, leading to a larger *p*-*d* band gap.

The unit-cell parameters of $Fe_yTi_{1-y}S_2$ reflect both the smaller size of Fe^{3+} relative to Ti^{4+} and the decreasing size of the S anion as it becomes oxidized. The latter is especially noticeable in the decrease of the *c*-axis parameter with increasing *y* (Fig. 2), while both factors contribute to the rapid decrease in the cell unit volume with increasing *y* (Fig. 4). Similar behavior is not seen in the Cr-substituted compounds, we believe, for two reasons. First, the holes are localized (these compounds are poor conductors), presumably leading to discrete monovalent and divalent sulfur. The divalent sulfur is larger than the monovalent, and holds the layers apart. Second, when compounds are driven from metallic to insulating states, their volumes usually expand (as in Fig. 4).

The oxidation of the sulfur without producing a disproportionation of valence and subsequent formation of sulfur-sulfur pairs as in pyrites is unusual but is supported by some recent observations on some copper-containing sulfides.[20] Photoemission measurements on such compounds clearly establish that the copper is monovalent, thus a substantial number of valence band holes must occur in such compounds as CuS and Tl_2CuS_2. This leads to *p*-type metallic conduction as observed.[21] It should be remembered, however, that the Cu compounds are stable phases, while the substituted $Ti_{1-y}M_{1-y}S_2$ phases are metastable. For example, when the Fe compound is heated to about 300 °C it decomposes into TiS_2 and FeS_2 exothermically. In FeS_2 all the sulfur atoms are monovalent and are joined to form covalently bonded sulfur-sulfur pairs, making the Fe divalent. Previous work also suggests that Se can also be oxidized in layered compounds such as $V_{0.5}Fe_{0.5}Se_2$.[22]

We note that the center shift of the two Fe sites in the metastable layered compound $Li_{0.17}FeS_2$ is close to 0.35 mm/sec.[23] From this observation and the previous discussion, it is likely that the Fe is trivalent and that the sulfur is significantly oxidized in $Li_{0.17}FeS_2$.

The electrochemical cell data of Fig. 12 show that the compounds with Fe substitution have a higher cell capacity than those with V or Cr substitution. The energy density of the former compounds is almost identical with that of TiS_2 itself. In the V and Cr compounds the cell capacity is much smaller than expected on the basis of the starting stoichiometry. However, this is probably not intrinsic; rather it is most likely due to interlayer pinning caused by antisite defects (transition metal on lithium sites). Such rapid reduction in cell capacity with small defect concentrations is well known. The defect concentration in the Fe compounds is lower and may be due to the fact that the preparation temperature is lower in this case. The cell performance is expected to improve if the defect level is reduced (or the stoichiometry improved) by lower temperature preparative techniques and if the particle size of the powders used to make cathodes is decreased. Cell reversibility beyond $x = 1$ was not good: only slightly better than that of TiS_2 in this range. The source of this irreversibility was not investigated in detail but may be due to extrinsic factors such as the particular electrolyte used.

SUMMARY

We have shown that substitution of Ti by other transition metals is possible in $LiTiS_2$ by high-temperature synthesis and that the lithium can be removed from these compounds at room temperature to form metastable layered compounds of the type $Ti_{1-y}M_yS_2$. These compounds irreversibly decompose at temperatures above 300 °C when $M = \mathrm{Fe}$ or Cr. When $M = \mathrm{V}$, the compounds are best described as alloys between TiS_2 and VS_2, both of which are normal layered compounds with divalent sulfur. Neither CrS_2 nor FeS_2 have been prepared as a pure (presumably metastable) layered phase. Their alloys with TiS_2, however, can be prepared for concentrations up to 0.75 and 0.66 for Cr and Fe, respectively. Cr is trivalent, independent of the amount of lithium intercalated between the layers. However, upon removal of Li, iron is oxidized from $2+$ (high spin) to $3+$ (low spin). Since the Cr or Fe is trivalent in the delithiated compounds, the sulfur must be oxidized. In the Fe case the oxidation is uniform leading to hole conduction in the sulfur valence band. This is somewhat unusual, in that in most sulfur compounds the oxidation is localized onto some of the sulfur to produce $1-$ valent species which then form covalent pairs, as in pyrites. Finally, since the compounds are layered, they can be used as cathodes in lithium batteries. The cell capacities of the Fe compounds are as good as that of TiS_2, but the capacities of the V and Cr compounds are smaller. There was no improvement in the cell reversibility beyond $x = 1$ that might have been expected from the recent studies of the electrochemical properties of Li_2FeS_2.[5] However, lower-temperature synthetic methods and different electrolytes may lead to reversible cathodes beyond $x = 1$.

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