

Structural and NMR Study of the Lithiated Defect Thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$)

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Received May 31, 1988

Oxidative extraction of copper from the normal thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ followed by chemical lithiation of the resulting defect thiospinel enabled the metallic, lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) to be prepared with high purity and chemical homogeneity. X-ray and neutron powder-diffraction studies of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) showed that lithium insertion into $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is topotactic and that the inserted lithium occupies only the 16c-octahedral sites of the thiospinel framework at all lithium compositions. Static and MAS ^7Li NMR spectra of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) exhibited a single lithium resonance with a small chemical shift relative to lithium acetate dihydrate at all lithium compositions; the chemical shift increased linearly with increasing lithium content, x . The ^7Li NMR spectra showed the onset of quadrupolar line broadening and a Knight-shift anisotropy for $x \geq 0.9$; these effects are probably due to interactions between lithium ions on neighboring edge-sharing 16c sites. © 1988 Academic Press, Inc.

Introduction

Two recent papers by Schöllhorn and Payer (1) and by Sinha and Murphy (2) reported that copper can be extracted topotactically from the normal spinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ with mild oxidizing agents at room temperature to give defect thiospinels of approximate composition $\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$. If the initial thiospinel was titanium-rich ($\text{Cu}_{0.8}\text{Ti}_{2.05}\text{S}_4$), then all of the copper could be extracted to give the novel, cubic titanium sulfide $c\text{-Ti}_{2.05}\text{S}_4$. It was further reported that up to

two equivalents of lithium could be inserted reversibly into $\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$ or $c\text{-Ti}_{2.05}\text{S}_4$, that the open-circuit voltages versus lithium metal of the lithiated defect thiospinels were comparable to that of layered Li_xTiS_2 over the whole lithium-composition range, and that the lithium-ion mobility in the lithiated defect thiospinels appeared to be high. The defect thiospinels are, therefore, of technical interest as possible cathode materials for lithium secondary batteries; for this purpose they would offer the following important advantages over layered TiS_2 : three-dimensional electronic and ionic conductivity, an isotropic lattice ex-

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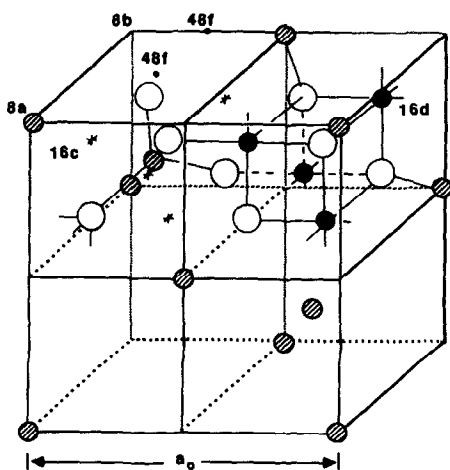


FIG. 1. The normal $A[B_2]X_4$ spinel structure.

pansion on lithium insertion, no tendency to intercalate water or solvent molecules from the electrolyte, and easy control of titanium stoichiometry.

The cubic, normal spinel structure $A[B_2]X_4$ is illustrated in Fig. 1. The unit cell contains 32 anions in a cubic-close-packed array (32e positions of the $Fd\bar{3}m$ space group). The A cations occupy the 8a tetrahedral interstices of the anion array and the B cations occupy the 16d octahedral interstices; in addition, there are empty 16c octahedral and 8b and 48f tetrahedral interstices. The 16c sites each share two faces with 8a sites to provide a continuously interconnected three-dimensional interstitial space within the $[B_2]X_4$ framework through which small ions such as lithium can diffuse; for example, the defect chlorospinel $\text{Li}_{0.8}[\text{Li}_{0.8}\text{Mg}_{1.2}]\text{Cl}_4$ is a lithium solid electrolyte with partial lithium-ion conductivity, $\sigma_{\text{Li}} = 5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ (3). However, the presence of A cations other than lithium impedes lithium-ion transport through the interstitial space; the alternative diffusion pathway via 48f sites requires a higher activation energy because these sites share two faces with occupied 16d sites. The 8b tetra-

hedral interstices share all four faces with 16d sites occupied by the B cations, so they are inaccessible to inserted lithium. Oxidative extraction of copper from $\text{Cu}[\text{Ti}_2]\text{S}_4$ creates a nearly ideal $[\text{Ti}_2]\text{S}_4$ defect spinel framework; the bottleneck size for ionic diffusion via 8a and 16c sites in such a framework is comparable to that in the chlorospinel, so fast lithium-ion diffusion in the defect thiospinel can be predicted.

The smooth variation in the open-circuit voltage versus lithium metal of $\text{Li}_x\text{Ti}_{2.05}\text{S}_4$ with no discontinuity at the normal spinel composition $\text{Li}_{1.0}\text{Ti}_{2.05}\text{S}_4$ led Sinha and Murphy (2) to propose that the inserted lithium occupies only the 16c-octahedral sites of the defect thiospinel framework at all lithium compositions, despite the fact that lithium occupancy of the 8a sites of the $[\text{Ti}_2]\text{S}_4$ framework (the normal spinel A cation sites) is electrostatically favored on a point-charge model for $x \leq 1.0$. Furthermore, it has been shown by neutron-diffraction experiments that the lithium in the oxospinel frameworks $\text{Li}_x[M_2]\text{O}_4$ ($M = \text{Ti}, \text{V},$ and Mn) (4–6) occupies only the 8a sites for $x \leq 1$; lithiation of the oxospinel frameworks beyond $x = 1$ gives rise to a gradual displacement of lithium ions from 8a to 16c sites because of electrostatic repulsion between ions on adjacent, face-sharing 8a and 16c sites with the result that $\text{Li}_2[\text{Ti}_2]\text{O}_4$, for example, has an ordered rocksalt structure with all of the lithium on the 16c sites (4).

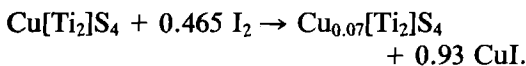
The objectives of this study were to prepare samples of the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ with high purity and chemical homogeneity, to locate the inserted lithium in these materials, and to study the effect of lithium insertion on the structure and bonding of the $[\text{Ti}_2]\text{S}_4$ framework by X-ray and neutron powder diffraction and ^7Li solid-state NMR.

1. Chemical Synthesis

The dark-green, metallic thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ was prepared by direct synthesis.

Copper powder (Johnson–Matthey, 150 mesh, 99.9%), titanium powder (Johnson–Matthey, 100 mesh, 99.9%), and sulfur granules (Aldrich, 99.999%) were mixed in stoichiometric proportion in an argon-filled glove box and sealed into a silica ampoule under high vacuum ($P < 10^{-4}$ Torr). The ampoule was heated at 350–450°C for 10 days to achieve complete reaction of the elemental sulfur and then at 750°C for 7 days. The product was recovered in an argon-filled glove box, ground, and sintered under high vacuum for a further 7 days at 750–800°C. The grinding and sintering was repeated once more in order to obtain highly pure and crystalline $\text{Cu}[\text{Ti}_2]\text{S}_4$.

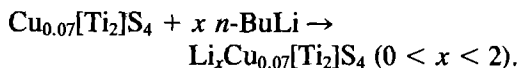
Oxidative extraction of copper from $\text{Cu}[\text{Ti}_2]\text{S}_4$ was achieved by vigorous stirring with a large excess of a 0.2 *M* solution of iodine in acetonitrile at 45°C for 21 days under a reduced pressure of dry nitrogen. The iodine solution was decanted and replaced every 7 days; the final product ($\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$, a dark-brown powder) was recovered with standard Schlenk techniques:



The copper iodide was readily removed since it is soluble in acetonitrile to the extent of 35 g l^{-1} at 35°C. Iodine/acetonitrile was preferable as an oxidizing agent to the $\text{FeCl}_3/\text{H}_2\text{O}$ or bromine/acetonitrile used previously (1, 2) because it is specific for the copper extraction reaction and shows no tendency to oxidize sulfide ions to sulfur. $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is the limiting composition for oxidative extraction of copper from $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$; the reason for this and a detailed account of the structure and bonding of the $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 < x < 0.93$) defect thiospinels are contained in a separate paper (7). $\text{Cu}[\text{Ti}_2]\text{S}_4$ and $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ are not appreciably air-sensitive, but all manipulations of these materials were carried out with the total exclusion of air and mois-

ture as a precaution against surface hydrolysis.

Chemical lithiation of the defect thiospinel $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ was carried out by vigorous stirring with controlled excess amounts of 0.1 *M* solutions of *n*-butyllithium in hexane at room temperature for 7 days under a reduced pressure of dry nitrogen:



The lithiation and product isolation were carried out with standard Schlenk techniques. The resulting material was pressed into pellets in an argon-filled glove box, sealed into Pyrex ampoules under high vacuum ($P < 10^{-4}$ Torr), and annealed at 250°C for 24 hr to give $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) with excellent purity and chemical homogeneity. The lithiated defect thiospinels are black, metallic powders that decompose slowly in air.

2. Powder-Diffraction Studies

X-ray powder-diffraction measurements were carried out on a Philips APD 3520 automated diffractometer; this instrument incorporates a Gaussian peak-fitting program for accurate location of diffraction peaks. Lattice parameters were refined with an iterative least-squares optimization program.

The neutron-diffraction profiles of 10-g samples of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($x = 0.93$ and 1.93) were obtained with the time-of-flight diffractometer GPPD at IPNS, Argonne. Structural parameters were refined from the diffraction profile with the Argonne Rietveld suite (8).

3. ^7Li Solid-State NMR

Static and MAS ^7Li NMR spectra of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ with $x = 0.35, 0.73, 0.90, 1.73,$ and 1.93 were measured at 77.73 MHz on a Bruker MSL 200 spectrometer; the reference material was lithium acetate dihydrate. MASNMR was carried out by encasing approximately 100 mg of the sample in

an alumina cylindrical rotor with a double-bearing probe and spinning it at up to 4.0 kHz. The 90° pulse length was $4 \mu\text{sec}$ and the preacquisition delay time in the MAS experiments was varied until it lay just on top of a rotational echo. The recycle delay time was 5 sec. Static ^7Li NMR spectra were obtained from larger samples (1–2 g); the quadruple-echo pulse sequence (9) was used in order to avoid phase distortions arising from the receiver dead time.

Results and Discussion

1. X-Ray and Neutron Powder Diffraction

Lithiation of the defect thiospinel $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ results in an isotropic lattice expansion; it does not otherwise alter the X-ray diffraction pattern. Figure 2 shows the cubic lattice parameter plotted against lithium composition, x . It can be seen that the lithiated defect thiospinel obeys Vegard's law within the limits of experimental error; this result is consistent with previously published data (2). The maximum isotropic expansion of the lattice is 3.1% (11.0% by volume); the corresponding layered titanium sulfide Li_xTiS_2 shows a similar volume expansion on lithiation, but this expansion is highly anisotropic and nonlinear (10). It should be noted that the expansion of the $[\text{Ti}_2]\text{S}_4$ framework on lithiation does not arise primarily from the size of the lithium ions, but from the simultaneous injection of electrons into the conduction band, which is antibonding with respect to titanium–sulfur interactions.

Samples of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($x = 0.93$ and 1.93) were submitted for neutron powder diffraction; their observed, calculated, and difference diffraction profiles are shown in Figs. 3 and 4, respectively. All of the peaks in the diffraction pattern could be indexed to the spinel structure; there were no additional peaks due to impurities or to superstructure ordering of the inserted lithium in

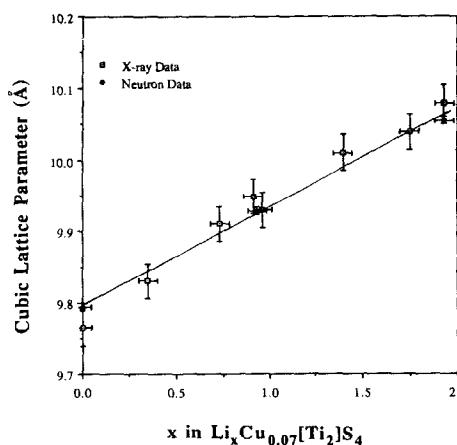


FIG. 2. The cubic lattice parameter of the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ as a function of lithium composition, x .

either of the samples. Despite some “tailing” of the diffraction peaks, which might be due to chemical inhomogeneity or to quasi-elastic scattering from the mobile lithium ions, Rietveld refinements of the structures converged rapidly to the parameters given in Table 1. Since the lithium and the residual copper occupy the same interstitial space in the structure, it was necessary to constrain the refinement of copper/lithium occupancies according to the stoichiometry of the compounds.

The outstanding feature of the refined structures is that the lithium occupies only the 16c-octahedral sites at both compositions. On an electrostatic point-charge model the lithium in $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is expected to occupy the 8a-tetrahedral sites (the normal spinel A cation sites); this electrostatic site preference is evidently outweighed by stronger Li–S covalent bonding on the 16c-octahedral sites. The reason why Li–S covalent bonding favors octahedral coordination is unclear. The corresponding oxospinel, $\text{Li}[\text{Ti}_2]\text{O}_4$, has been shown by neutron powder diffraction to have lithium on the 8a sites only (4); the difference between the oxo- and thiospinels

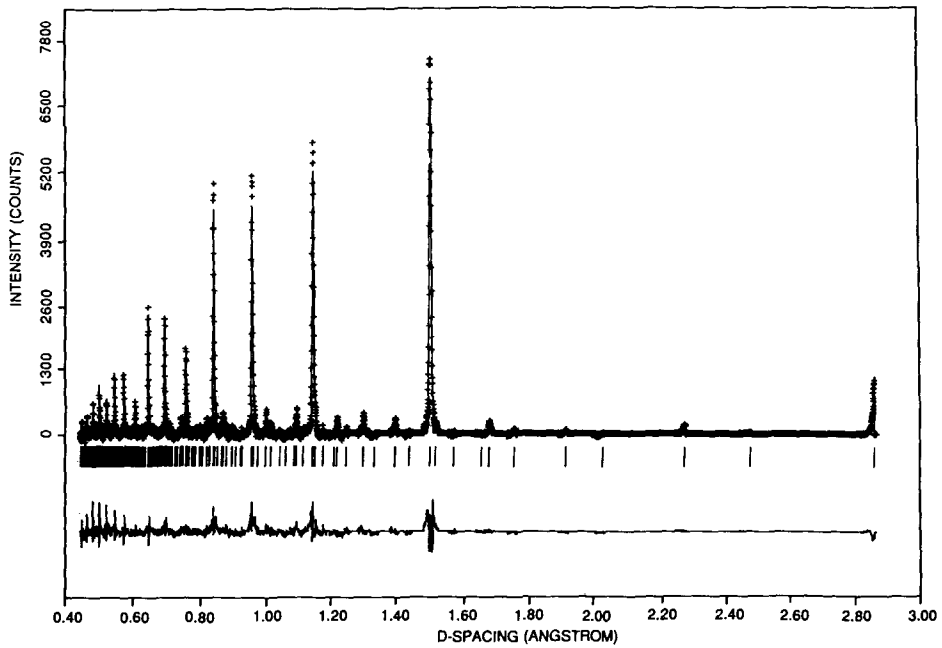


FIG. 3. Neutron powder-diffraction pattern of $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$. Observed data are shown by crosses; calculated and difference profiles are shown by solid lines.

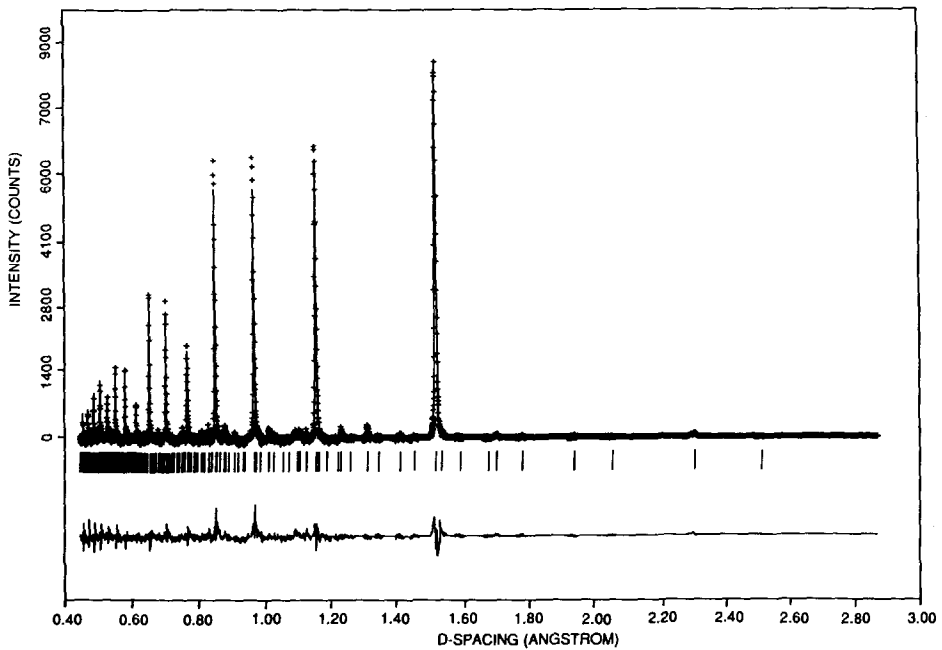


FIG. 4. Neutron powder-diffraction pattern of $\text{Li}_{1.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$. Observed data are shown by crosses; calculated and difference profiles are shown by solid lines.

TABLE I
STRUCTURAL PARAMETERS OF THE LITHIATED
DEFECT THIOSPINELS REFINED FROM NEUTRON
POWDER-DIFFRACTION DATA

Atom	Position	x/a	y/b	z/c	B_{iso}	Occupancy
(a) $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$						
Space group $Fd\bar{3}m$; $a = b = c = 9.9286$ (0.0003) Å						
S	32e	0.2538	0.2538	0.2538	0.38 (0.02)	32.0 (0.0)
Ti	16d	0.5000	0.5000	0.5000	0.51 (0.02)	16.0 (0.0)
Cu(1)	8a	0.8750	0.8750	0.8750	1.4 (0.1)	0.3 (0.1)
Cu(2)	16c	0.0000	0.0000	0.0000	—	0.0 (0.0)
Li(1)	8a	0.8750	0.8750	0.8750	—	0.0 (0.0)
Li(2)	16c	0.0000	0.0000	0.0000	0.88 (0.02)	7.4 (0.1)
$R_p = 4.1\%$, $R_{wp} = 6.0\%$, $R_{wp}(\text{expected}) = 2.7\%$						
(b) $\text{Li}_{1.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$						
Space group $Fd\bar{3}m$; $a = b = c = 10.0554$ (0.0002) Å						
S	32e	0.2544	0.2544	0.2544	0.24 (0.02)	32.0 (0.0)
Ti	16d	0.5000	0.5000	0.5000	0.60 (0.02)	16.0 (0.0)
Cu(1)	8a	0.8750	0.8750	0.8750	—	0.0 (0.0)
Cu(2)	16c	0.0000	0.0000	0.0000	0.57 (0.02)	0.3 (0.1)
Li(1)	8a	0.8750	0.8750	0.8750	—	0.0 (0.0)
Li(2)	16c	0.0000	0.0000	0.0000	0.57 (0.02)	15.5 (0.1)
$R_p = 3.8\%$, $R_{wp} = 5.3\%$, $R_{wp}(\text{expected}) = 2.8\%$						

Note. The standard deviations of refinable parameters are given in parentheses. The standard deviation of the sulfide x , y , z parameter in both (a) and (b) was 0.0002. The R factors are defined as $R_p = 100[\sum_{i=1}^N |Y_i(\text{obs}) - Y_i(\text{calc})| / \sum_{i=1}^N Y_i(\text{obs})]$, $R_{wp} = 100[\sum_{i=1}^N |w_i Y_i(\text{obs}) - Y_i(\text{calc})|^2 / \sum_{i=1}^N w_i Y_i^2(\text{obs})]^{1/2}$, $R_{wp}(\text{expected}) = 100[(N - P + C) / \sum_{i=1}^N w_i Y_i^2(\text{obs})]^{1/2}$, where Y_i = number of counts at the i th data point, w_i = weighting factor for the i th data point, N = number of statistically independent observations, P = number of least-squares parameters in the refinement, C = number of constraint functions in the refinement.

is accounted for by the higher Madelung energies in the oxide, which increases the electrostatic 8a-site preference in the oxide, combined with the fact that Li–O covalent bonding is weaker than Li–S covalent bonding, which reduces the covalent 16c-site preference.

The octahedral-site preference of lithium in the thiospinel framework explains why the hypothetical lithium thiospinel $\text{Li}[\text{Ti}_2]\text{S}_4$ cannot be prepared at high temperature; it is thermodynamically unstable with respect to the layered phases TiS_2 and LiTiS_2 . (Interestingly, it has been reported that $\text{Li}_{0.5}\text{ZrS}_2$ prepared by chemical lithiation of layered ZrS_2 spontaneously transforms into the thiospinel $\text{Li}[\text{Zr}_2]\text{S}_4$ on heating to 600°C; the lithium ions have not yet been located in this material (11, 12).)

The high quality of the diffraction data enabled the residual copper to be located in both of the lithiated phases. It occupies the tetrahedral 8a sites (the normal spinel A cation sites) in $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$, but is displaced to the 16c-octahedral sites in $\text{Li}_{1.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$; this displacement is due to electrostatic repulsion between copper atoms on 8a sites and inserted lithium ions on neighboring face-sharing 16c sites. Similar displacements of A cations have been observed as a result of lithium insertion into normal spinels such as $\text{Cu}[\text{Zr}_2]\text{S}_4$ (13), Fe_3O_4 (14), and Mn_3O_4 (15).

Finally, we note that the sulfide anion position parameter is 0.253–0.254 for the lithiated defect thiospinels $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ and $\text{Li}_{1.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$; the corresponding parameter in $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is 0.251. This result implies that lithiation results in a small expansion of the 16c sites (the LiS_6 octahedra) relative to the 16d sites (the TiS_6 octahedra).

2. ^7Li NMR of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$)

The principal features of the ^7Li NMR spectra can be summarized as follows:

—All of the lithiated defect thiospinels exhibited a single ^7Li resonance with a small chemical shift relative to lithium acetate dihydrate. The chemical shift increased linearly with lithium content, x , from -4.45 ppm at $x = 0.35$ to $+12$ ppm at $x = 1.93$ (Fig. 5).

—The full width at half height (FWHH) of the lithium resonance in static NMR increases in a nonlinear fashion with increasing lithium content from 600 Hz at $x = 0.35$ to 7.6 kHz at $x = 1.93$ (Fig. 6).

—Strong and asymmetric spinning sidebands appear in the ^7Li MASNMR spectra for $x \geq 0.90$; representative spectra are shown in Fig. 7.

—The FWHH of the central lithium resonance in MASNMR also increases with in-

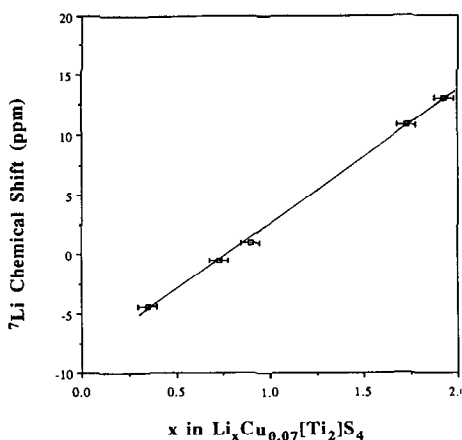


FIG. 5. ^7Li NMR chemical shift in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ as a function of lithium composition, x .

creasing lithium content from 200 Hz at $x = 0.35$ to 1 kHz at $x = 1.93$.

In the interpretation of the NMR spectra it is necessary to take into account the three major interactions that characterize the behavior of these spin systems. These are the chemical shift or Knight shift for a metal, the quadrupole interaction, and the dipole-dipole coupling. For lithium the chemical shift range is rather small, less than 4 ppm. Larger paramagnetic changes in the resonant frequency can be identified as a Knight shift caused by conduction-band electron density at the lithium nuclei; for example, the Knight shift in metallic lithium is +250 ppm. No clear-cut method exists for differentiating between the chemical shift and the Knight shift. Dipole-dipole coupling can be an important source of line broadening, but for these phases the contribution to the line width is relatively small; most importantly, we can neglect the contributions from dipole-dipole coupling to both sulfur and the titanium as the overwhelmingly abundant spin for S is $I = 0$ and Ti has only a small gyromagnetic ratio. The dipole-dipole coupling between lithium ions should also be comparatively small, since lithium ions in

adjacent 16c sites of the spinel framework are 3.6 Å apart; it can be calculated that the dipole-dipole interaction between two lithium ions 3.6 Å apart amounts to only 220 Hz. In a large range of systems—including lithium glasses, lithium in zeolites, and lithium-ion conductors such as Li_3N —the dominant interaction is the lithium quadrupolar interaction. Typical lithium quadrupole coupling constants are less than 100 kHz and, even in sites grossly distorted from cubic symmetry, do not exceed 500 kHz. This is extremely useful since it means that first-order perturbation theory is sufficient to describe the quadrupolar term in the Hamiltonian interaction. In this work we can only offer a qualitative interpretation of the data; additional experiments involving the determination of the lithium-ion mobility are necessary to be quantitative.

The static ^7Li NMR spectrum of $\text{Li}_{0.35}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is characterized by a sharp resonance with a Lorentzian lineshape and a FWHH of less than 500 Hz. There was no indication of a quadrupole interaction either by the presence of resolved satellite transitions or a broad Gaussian com-

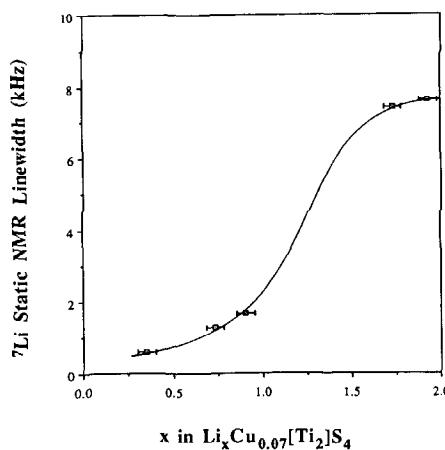


FIG. 6. Static ^7Li NMR linewidth in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ as a function of lithium composition.

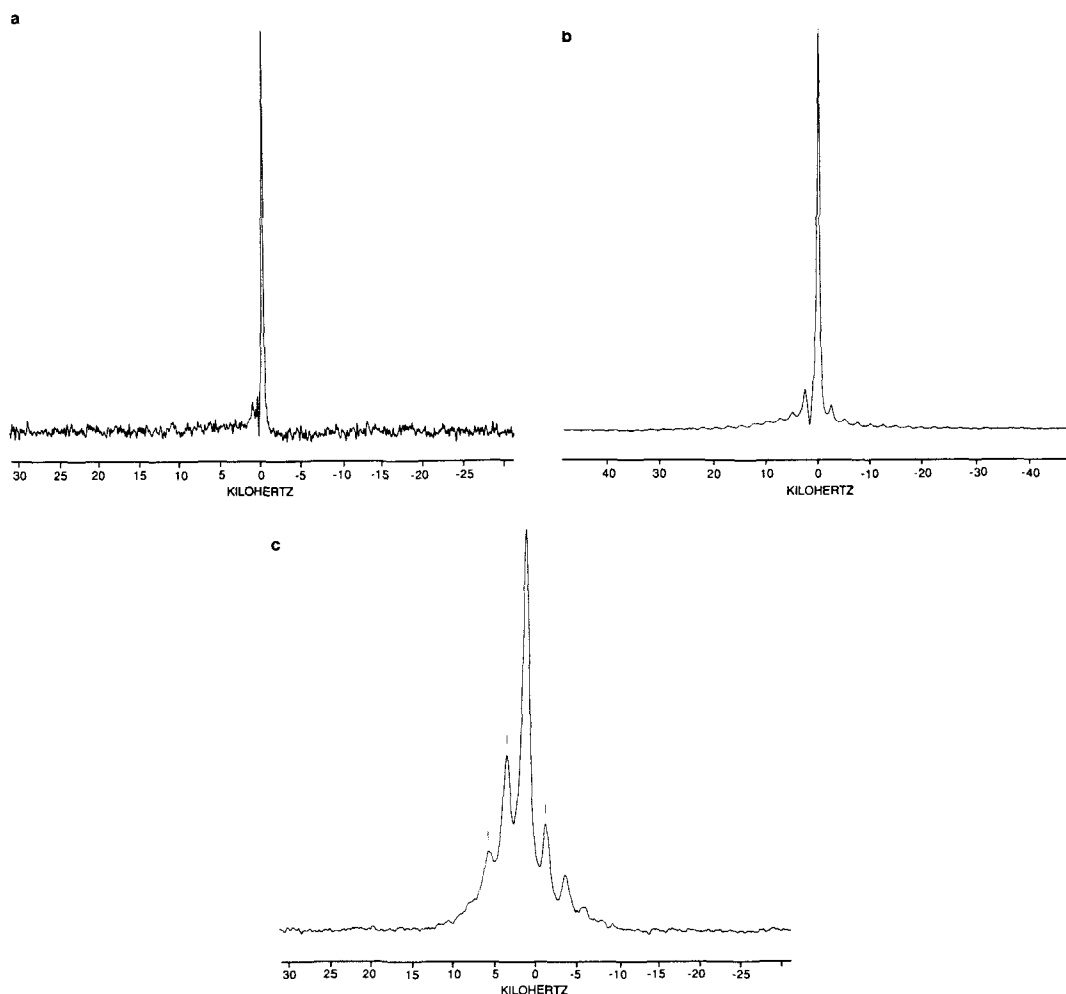


FIG. 7. $^7\text{MASNMR}$ spectra of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$; (a) $x = 0.35$, (b) $x = 0.90$, (c) $x = 1.93$.

ponent to the lineshape. The narrow linewidth of the observed resonance rules out the possibility of a very large quadrupolar coupling as this would give rise to second-order broadening of the central $1/2 \rightarrow -1/2$ transition. We can conclude that the very small trigonal distortion from ideal octahedral symmetry of the 16c sites (site symmetry $3m$) is not sufficient to cause significant quadrupolar line broadening. An accurate determination of the resonant frequency is possible by MASNMR, which narrows the linewidth to only 200 Hz by

averaging the dipole-dipole coupling. The chemical shift is -4.45 ppm with respect to lithium acetate dihydrate at 0.0 ppm; such a chemical shift is typical of nonmetallic systems and indicates that the conduction-electron density at the lithium nuclei in $\text{Li}_{0.35}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is effectively zero. It provides direct evidence of electron transfer from the lithium to the $[\text{Ti}_2]\text{S}_4$ host matrix. As the lithium-ion concentration in the defect thiospinel is increased, the lithium chemical shift becomes more paramagnetic. At the maximum lithium composi-

tion, $x = 1.93$, the chemical shift of +12 ppm is no longer typical of a nonmetallic phase, though it should be noted that the conduction-electron density at the lithium nuclei is still small.

Increasing the lithium-ion concentration in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ also increases the static NMR linewidth of the ^7Li resonance. A Knight-shift dispersion, second-order quadrupolar, and the dipolar effects can all be ruled out as the principal cause of the linewidth because the broad resonance at $x = 1.93$ breaks up into a series of sidebands at a spinning speed far less than the resonance linewidth, implying that the interaction causing the linewidth is anisotropic. From this we can infer that the increase in the resonance linewidth is caused primarily by a Knight-shift anisotropy with the characteristic lineshape being disguised by broadening from quadrupolar and dipolar coupling; even after MAS, the isotropic resonance at $x = 1.93$ has a FWHH of about 1 kHz. Support for this model is provided by a detailed examination of the static quadrupole-echo NMR spectrum at $x = 0.90$, which indicates that the reduction in symmetry also gives a quadrupolar interaction; curve fitting of the lineshape indicates a narrow component, FWHH = 2.0 kHz, and a broad, underlying component, FWHH = 12.2 kHz, in the intensity ratio 5:3. This ratio is close to the required ratio of 3:2 if the broad component represents satellite transitions of a quadrupolar interaction. The presence of the broad, underlying component is highlighted in the MASNMR spectra and in particular at the high spinning speeds where the dipolar coupling has been averaged to zero, leaving only the quadrupolar term. A more complete analysis of the quadrupolar contribution is greatly hampered by the broad nature of the static spectrum, but the spinning sideband distribution suggests a value of about 20 kHz with an asymmetry of 1.0. It is difficult to say whether the quadrupolar coupling is changing with composition; be-

low $x = 0.73$ there is no evidence whatsoever, while at the higher $x = 1.73$ composition it appears that the Knight-shift anisotropy has increased to the extent that the broad, underlying peak is not obvious.

The onset of a weak quadrupolar interaction (~ 20 kHz) and a Knight-shift anisotropy of the ^7Li resonance in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ for $x \geq 0.90$ is to be expected due to a reduction in the symmetry of the electronic environment of the lithium ions arising from occupation of the neighboring edge-sharing 16c sites by other lithium ions. An interesting feature of the spectra is that significant effects due to Li-Li interactions do not appear at lower lithium contents; based on an analysis of the distribution of the 16c sites in three dimensions and assuming avoidance of lithium nearest-neighbors, Li-Li pairs should be present for all $x > 0.5$. A likely explanation is that rapid lithium-ion hopping results in an averaging out of Li-Li interactions at lower lithium contents. Electrochemical measurements have shown that the lithium-ion self-diffusion coefficient (D_{Li}) in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0.5 \leq x \leq 1.5$) is approximately $1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at room temperature (16); on a simple, three-dimensional random-walk model this corresponds to a lithium-ion hopping frequency of approximately 1 MHz. The lithium-ion hopping frequency in layered Li_xTiS_2 , determined by temperature-dependent NMR, is approximately 4 MHz at room temperature (18). Such hopping frequencies would be sufficient to effectively average out any anisotropic Knight shift or quadrupole interaction at low lithium contents. The anisotropic interactions that are clearly evident for samples of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ with $x \geq 0.90$ are observable because the lithium ions in these materials are hopping between sites with identical anisotropy.

The ^7Li static NMR spectra of the $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ lithiated defect thiospinels have many features in common with the previously measured spectra of the lithiated layered sulfides Li_xTiS_2 ($0 < x < 1$).

Silbernagel and Whittingham (17) reported that the ^7Li chemical shift in Li_xTiS_2 increases linearly from +3 ppm ($x = 0.1$) to +12 ppm ($x = 1.0$), relative to a LiI solution at 0.0 ppm. They were also able to obtain quadrupole coupling constants by measuring the splitting between the principal and quadrupole satellite transitions (these are not resolved for the defect thiospinels); the coupling constants also increased linearly with x , from 7 kHz at $x = 0.2$ to ~ 30 kHz at $x = 1$. Since the variation in the c/a lattice-parameter ratio of Li_xTiS_2 is highly nonlinear in x , the linear increase in the quadrupole coupling constant implies that the quadrupolar broadening of the lithium resonance is not due primarily to distortion of the Li sites from ideal octahedral symmetry due to c -axis dilation, but instead is caused by Li-Li interactions. This conclusion is supported by the observation of Silbernagel that the magnitude of the ^7Li quadrupolar line broadening is very similar in a wide range of LiMS_2 and LiMSe_2 phases ($M = \text{Ti, Zr, Hf, Ta, Nb}$) (18), and by the observation of Eguchi *et al.* (19) that the quadrupolar coupling constant of $\text{Li}_{0.94}\text{TiS}_2$ is independent of pressure up to 5 kbar. Since the trigonal distortion of the lithium sites in the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is even less than that in the layered sulfides, we can conclude that the quadrupolar broadening and Knight-shift anisotropy of the ^7Li resonance in the lithiated defect thiospinels are also due primarily to Li-Li interactions.

The ^7Li NMR spectra of $\text{Li}_{0.90}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ appeared unaffected by raising the temperature from 293 to 360 K. However, a variable-temperature study of the ^7Li relaxation times would provide valuable information on the mechanism of the observed line broadening and the activation energy for lithium-ion hopping.

Acknowledgments

This work has benefited from the use of the Intense Pulsed Neutron Source at Argonne National Labora-

tory. This facility is funded by the U.S. Department of Energy, BES-Materials Science, under Contract W-31-109-Eng-38.

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