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# CHARACTERIZATION OF DEFECT THIOSPINELS $Cu_{1-x}[Ti_2]S_4$ (0<x≤0.93)

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# ABSTRACT

The thiospinel framework [Ti<sub>2</sub>]S<sub>4</sub> represents a metastable host selective to Li insertion/extraction reactions in three dimensions that is of technical interest as a battery-cathode material. Synthesis is performed by oxidative extraction of copper from Cu[Ti2]S4, but complete extraction of copper from a stoichiometric starting material has not been possible. We report structural, transport, magnetic, <sup>65</sup>Cu NMR, and electrochemical data for the defect-thiospinel systems Cu<sub>1-x</sub>[Ti<sub>2</sub>]S<sub>4</sub>,  $0 < x \le 0.93$ , obtained by extracting copper with I<sub>2</sub> at 45 °C. X-ray data show a linear decrease in lattice parameter with increasing x up to 2.4% (7.2% by volume) at  $Cu_{0.07}[Ti_2]S_4$ . Neutron diffraction shows the residual copper atoms of the x = 0.93 sample remain in the tetrahedral 8a sites of the spinel framework. All samples are metallic or semimetallic and Pauli paramagnetic; <sup>65</sup>Cu NMR resonance exhibits a large Knight shift for all x, which indicates an important Cu-4s character at the Fermi energy in the conduction band. Electrochemical lithiation of Cu[Ti2]S4 and  $Cu_{0.07}$ [Ti<sub>2</sub>]S<sub>4</sub> gave an open-circuit voltage versus lithium that is higher in the former than it is in the latter. These several properties, including the limiting composition x = 0.93, are accounted for by constructing semi-empirical band diagrams for Cu[Ti<sub>2</sub>]S<sub>4</sub> and Cu<sub>0.07</sub>[Ti<sub>2</sub>]S<sub>4</sub>.

### MATERIALS INDEX: thiospinels

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#### Introduction

Framework structures that incorporate a continuously interconnected three-dimensional interstitial space into which electroactive ions can be inserted and through which such ions can diffuse are of interest as solid electrolytes (e.g. NASICON Na<sub>3</sub>Zr<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub>PO<sub>4</sub>, [1]) and as cathode materials for secondary batteries (e.g. Li<sub>x</sub>Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>2</sub>, [2]). The [B<sub>2</sub>]X<sub>4</sub> subarray of a normal A[B<sub>2</sub>]X<sub>4</sub> spinel incorporates such an interstitial space comprised of face-sharing 8a tetrahedral interstices (the A-cation sites of the normal spinel) and 16c octahedral interstices. However, the small, triangular bottlenecks between these sites limits fast diffusion in spinel frameworks to small ions such as lithium. Lithium insertions into oxospinel frameworks, including Li[Ti<sub>2</sub>]O<sub>4</sub> [3],  $\lambda$ -MnO<sub>2</sub> [4], and Li[V<sub>2</sub>]O<sub>4</sub> [5] have been studied in detail; it appears that the bottleneck size in such frameworks is too small to allow fast lithium-ion diffusion. However, fast lithium-ion diffusion has recently been observed in the defect chlorospinel Li<sub>0.8</sub>[Li<sub>0.8</sub>Mg<sub>1.2</sub>]Cl<sub>4</sub> ( $\sigma$ <sub>Li</sub>=5 x 10<sup>-5</sup> Ω<sup>-1</sup>cm<sup>-1</sup> at 293 K) [6]. We can thus predict the occurrence of fast lithium-ion diffusion in thiospinel frameworks [M<sub>2</sub>]S<sub>4</sub>, since the sulfide-ion radius is similar to that of the chloride ion.

The octahedral-site preference of lithium in sulfides means that thiospinels of formula  $Li[M_2]S_4$ , where M is a transition metal of the first or second series, are thermodynamically unstable with respect to layered phases. However, normal thiospinels  $Cu[M_2]S_4$  with M=Ti, Zr, V, Cr, Co, Ni, and Rh can be prepared, and lithium insertion into some of these materials has been studied [7,8]. Up to one equivalent of lithium could be inserted chemically or electrochemically into  $Cu[Ti_2]S_4$  and  $Cu[Zr_2]S_4$ , but the lithium-ion mobility in the lithiated thiospinels was found to be low because the copper atoms block the optimum diffusion pathway for lithium. Removal of the copper, leaving the  $[M_2]S_4$  framework intact, would be expected to enable more lithium to be inserted and greatly increase the lithium-ion diffusion rate.

Le Nagard *et al.* described the preparation of copper-deficient thiospinels  $Cu_{1-x}[Ti_2]S_4$ (x $\leq 0.44$ ) by direct synthesis at high temperature [9]. More recently, two papers by Schöllhorn and Payer [10] and by Sinha and Murphy [11] have reported that up to 90% of the copper can be extracted topotactically from  $Cu[Ti_2]S_4$  with mild oxidizing agents at room temperature:

Cu[Ti <sub>2</sub> ]S <sub>4</sub>	+	FeCl <sub>3</sub> /H <sub>2</sub> O	$\rightarrow$	Cu <sub>0.1</sub> [Ti <sub>2</sub> ]S <sub>4</sub>	+	CuCl <sub>2</sub> /FeCl <sub>2</sub> /H <sub>2</sub> O	[10],
Cu[Ti <sub>2</sub> ]S <sub>4</sub>	+	Br <sub>2</sub> /CH <sub>3</sub> CN	$\rightarrow$	Cu <sub>0.1</sub> [Ti <sub>2</sub> ]S <sub>4</sub>	+	CuBr/CH <sub>3</sub> CN	[11].

If the starting material was slightly titanium-rich ( $Cu_{0.8}Ti_{2.05}S_4$ ), then all of the copper could be extracted to give the novel, cubic titanium sulfide  $c-Ti_{2.05}S_4$ . Up to two equivalents of lithium could be inserted chemically or electrochemically into  $Cu_{0.1}[Ti_2]S_4$  and  $c-Ti_{2.05}S_4$ . The opencircuit voltage of the lithiated materials versus lithium metal was comparable to that of layered  $Li_xTiS_2$  over the whole lithium-composition range, and the lithium-ion mobility in the lithiated defect thiospinels appeared to be high; these materials are, therefore, of technical interest as possible substitutes for TiS<sub>2</sub> cathodes in lithium secondary batteries.

The objectives of this study were, first, to determine the effect of copper extraction on the structure and bonding of the  $[Ti_2]S_4$  framework of  $Cu_{1-x}[Ti_2]S_4$  and, second, to determine the nature of the residual copper at the limiting composition  $Cu_{0,1}[Ti_2]S_4$ . The observation that not all of the copper could be extracted from  $Cu[Ti_2]S_4$  could be due to one or more of the following reasons:

- The residual copper could be present as a separate phase, e.g. Cu<sub>2</sub>S.
- The residual copper could be trapped at defects or grain boundaries, or it could be located at special sites in the spinel structure; for example, it could have replaced some of the titanium on 16d-octahedral sites.

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- The starting material could be slightly titanium deficient, with the result that "Cu<sub>0.1</sub>[Ti<sub>2</sub>]S<sub>4</sub>" is in fact a semiconductor, Cu+<sub>0.1</sub>[Ti<sup>4+</sup>1.975]S<sub>4</sub>; no further copper can be extracted by oxidation because there are no oxidizable electrons in the predominantly Cu:4s-Ti:3d conduction band.
- Oxidative extraction of copper from Cu<sub>0.1</sub>[Ti<sub>2</sub>]S<sub>4</sub> could be impossible because the electrons at the Fermi energy in this material have sufficient sulfide-3p character to make oxidation of sulfide ions to sulfur the preferred oxidation process at this composition.

The experimental data, presented below, indicate that the last explanation is the correct one.

#### Experimental

The metallic, normal thiospinel  $Cu[Ti_2]S_4$  was prepared by direct synthesis from the elements at 350-750 °C under high vacuum in sealed, silica ampules. Repeated grinding and sintering at 750 °C ensured a product of good crystallinity and chemical homogeneity.

Oxidative extraction of copper from  $Cu[Ti_2]S_4$  was undertaken by vigorous stirring with a controlled excess of 0.1-0.2 M solutions of iodine in dry acetonitrile at 45 °C for 7-21 days under a reduced pressure of dry nitrogen. Iodine is preferable to the bromine or FeCl<sub>3</sub> solutions used previously [10,11] because it is specific for the copper-extraction reaction and shows no tendency to oxidize sulfide ions:

 $Cu[Ti_2]S_4 + (x/2)I_2/CH_3CN \rightarrow Cu_{1-x}[Ti_2]S_4 + xCuI$ 

The CuI is readily removed since it is soluble in acetonitrile to the extent of 35 g/l at 35  $^{\circ}$ C. The defect thiospinels were annealed at 150  $^{\circ}$ C for 48 hours under high vacuum to ensure chemical homogeneity. The resulting brown powders were not appreciably air sensitive, but all manipulations of these materials were carried out in an argon-filled glove box as a precaution against surface hydrolysis.

The limiting composition for oxidative copper extraction from  $Cu[Ti_2]S_4$  was found to be  $Cu_{0.07}[Ti_2]S_4$ ; continued reaction with iodine at elevated temperature and pressure, or with stronger oxidizing agents such as bromine, did not result in any further copper extraction. Electron microprobe analysis of  $Cu_{0.07}[Ti_2]S_4$  showed that the copper was not present in a separate phase, but was uniformly distributed through the product particles.

#### **Diffraction Measurements**

X-ray powder diffraction measurements were carried out with a Philips APD3520 powder 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. Observed X-ray diffraction patterns were compared with calculated patterns obtained with the program Lazy/Pulverix [12].

The neutron powder-diffraction profile of a 10 g sample of  $Cu_{0.07}[Ti_2]S_4$  was obtained on the time-of-flight diffractometer GPPD at IPNS, Argonne. Structural parameters were refined from the diffraction profile with the Argonne Rietveld suite [13].

#### Magnetic Susceptibility and <sup>65</sup>Cu NMR Measurements

The magnetic susceptibilities of samples of  $Cu_{1-x}[Ti_2]S_4$  with x=0, 0.25, 0.75, and 0.93 were measured with a Cahn Instruments Faraday balance in the temperature range 77-293 K. The

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sample size was approximately 10 mg. The instrument was calibrated with Hg[Co(NCS)<sub>4</sub>] ( $\chi_{p}$ =16.44 x 10<sup>-6</sup> emu g<sup>-1</sup> at 293 K) before each measurement.

Static <sup>65</sup>Cu NMR spectra of samples of Cu<sub>1-x</sub>[Ti<sub>2</sub>]S<sub>4</sub> with x=0, 0.25, 0.75, and 0.93 were measured at 56.79 MHz on a Bruker MSL 200 spectrometer at room temperature. The <sup>65</sup>Cu nucleus was studied in preference to the more abundant <sup>63</sup>Cu nucleus in order to avoid interference from folded-in <sup>23</sup>Na signals from the glass sample holder. The sample size was 2-3 g. A 4  $\mu$ s radiating r.f. pulse was used with an appropriate recycle time to avoid saturation effects. In all cases the spectra were acquired with a quadrupole-echo pulse sequence [21] with an interpulse spacing of 10  $\mu$ s, thereby overcoming phase distortions due to the receiver dead time. The spinlattice relaxation time, T<sub>1</sub>, for the <sup>65</sup>Cu nuclei was measured by the inversion recovery method.

#### Open-circuit Voltage (OCV) Measurements

Electrochemical lithiations of  $Cu[Ti_2]S_4$  and  $Cu_{0.07}[Ti_2]S_4$  were carried out in the cell of figure 1. Finely ground thiospinel (about 20 mg) was pressed at 10 tons pressure onto a 1-cmdiameter grid cut from 60-mesh stainless-steel gauze and assembled into the cell of figure 1 in an argon-filled glove-box. The electrolyte was a 1 M solution of LiBF<sub>4</sub> in purified propylene carbonate impregnating Whatman glass-fiber pads. The whole assembly was compressed by screwing together the stainless-steel spigots until a stable voltage was obtained between the cathode and the counter and reference electrodes. Lithium insertion was carried out by galvanostatic discharging at 10-20  $\mu$ A; the lithium was inserted stepwise, and the cell was allowed to equilibrate for 7-14 days at each lithium composition before the open-circuit voltage was measured.



FIG.1: Electrochemical cell for open-circuit voltage measurements.

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#### <u>Results</u>

# Structure of $Cu_{1-x}[Ti_2]S_4$ ( $0 \le x \le 0.93$ )

The cubic lattice parameters of the defect thiospinels  $Cu_{1-x}[Ti_2]S_4$  are shown in figure 2 along with the lattice parameters obtained by Le Nagard *et al.* [9] for the defect phases  $Cu_{1-x}$  $[Ti_2]S_4$  (x≤0.44) prepared at high temperature. The defect thiospinels clearly obey Vegard's Law with an isotropic, linear contraction of the lattice of up to 2.4% (7.2% by volume) as the copper is extracted. The X-ray diffraction pattern of  $Cu_{0.7}[Ti_2]S_4$  prepared at high temperature by direct synthesis is identical to that of  $Cu_{0.7}[Ti_2]S_4$  prepared by low-temperature extraction of copper from  $Cu[Ti_2]S_4$ . The observed X-ray diffraction-peak intensities of the  $Cu_{1-x}[Ti_2]S_4$  phases agree well with calculated values. However, X-ray powder diffraction cannot be used to locate the residual copper in  $Cu_{0.07}[Ti_2]S_4$  since the intensity of X-ray scattering from copper in this material is only 0.5% of that from the copper in  $Cu[Ti_2]S_4$ .



FIG 2: Cubic lattice parameter of  $Cu_{1-x}[Ti_2]S_4$  as a function of x.

The observed, calculated, and difference neutron-diffraction profiles of  $Cu_{0.07}[Ti_2]S_4$  are given in figure 3. The Rietveld refinement of the structure converged rapidly to the parameters given in Table I; the very high-quality data set, reflected in the low profile R-factors, enabled the residual copper to be located in the spinel framework: at least 60% of the residual copper is still giving rise to coherent scattering from the 8a tetrahedral sites (the A-cation sites of the normal spinel). We can conclude that there is no structural reason why this copper cannot be extracted. The refinement also indicates that all of the 16d octahedral sites (the B-cation sites of the normal spinel) are exactly filled by titanium, which suggests that the presence of residual copper is not due

to a titanium deficiency in the starting material. The high isotropic atomic temperature factors generated by the refinement probably reflect small, random distortions of the structure due to the residual copper. Finally, we note that the sulfide-ion position parameter in  $Cu_{0.07}[Ti_2]S_4$  is reduced to 0.251 from 0.257 in  $Cu[Ti_2]S_4$ ; this implies an enlargement of the 16d octahedral sites relative to the 8a tetrahedral sites and is entirely consistent with removal of copper atoms from the 8a sites.



FIG. 3: Powder neutron-diffraction pattern of  $Cu_{0.07}[Ti_2]S_4$ . Observed data as crosses; calculated and difference profiles as solid lines.

# TABLE I Structural Paramaters of Cu<sub>0.07</sub>[Ti<sub>2</sub>]S<sub>4</sub> Refined From Neutron Powder-Diffraction Data

# Space Group Fd3m; a=b=c=9.7492 (0.0000) Å

Atom	<b>Position</b>	<u>x/a</u>	<u>y/b</u>	<u>z/c</u>	<u>B</u> iso	<u>Occupancy</u>
S	32e	0.2513	0.2513	0.2513	0.66 (0.03)	32.0 (0.0)
L1 Cu	16d 8a	0.5000 0.8750	0.5000	0.5000	1.00 (0.05)	0.3 (0.1)

The standard deviation of the sulfide x,y,z prameter was 0.0001; standard deviations of other refinable parameters are given in brackets.

 $R_p = 3.2\%$   $R_{wp} = 4.4\%$   $R_{wp}(expected) = 2.7\%$ 

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The R-factors in Table I are defined as follows:

$$R_{p} = 100 \frac{\sum |Y_{i}(obs) - Y_{i}(calc)|}{\sum Y_{i}(obs)} \qquad R_{wp} = 100 \left[ \frac{\sum w_{i} |Y_{i}(obs) - Y_{i}(calc)|^{2}}{\sum w_{i} Y_{i}^{2}(obs)} \right]^{2}$$

$$R_{wp}(expected) = 100 \left[ \frac{(N - P + C)}{\sum w_i Y_i^2(obs)} \right]^{1/2}$$

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.

#### <u>Magnetic Susceptibility of $Cu_{1-x}[Ti_2]S_4$ ( $0 \le x \le 0.93$ )</u>

The magnetic susceptibilities of samples of  $Cu_{1-x}[Ti_2]S_4$  with x=0, 0.25, 0.75, and 0.93 in the temperature range 77-293 K are given in Table II, where the  $\chi_m$  are the measured molar susceptibilities and the  $\chi_s$  are the residual susceptibilities after subtraction of the atomic diamagnetism. All of the samples exhibited weak paramagnetism. The paramagnetism of the copper-deficient samples was temperature-independent within the limits of experimental error, but that of  $Cu[Ti_2]S_4$  decreases slightly with increasing temperature. The values of  $\chi_s$  for the copperdeficient materials are typical of Pauli paramagnetism due to conduction electrons in metals. The susceptibility of  $Cu_{1-x}[Ti_2]S_4$  decreases slightly as copper is extracted because electrons are simultaneously being removed from the conduction band; the elementary theory of Pauli paramagnetism predicts that  $\chi_s \propto N^{1/3}$  for a parabolic conduction band, where N is the number of conduction electrons. The paramagnetism of the limiting copper-deficient composition  $Cu_{0.07}[Ti_2]S_4$  suggests that this material is metallic or semimetallic; for comparison, stoichiometric TiS<sub>2</sub>, which is a small-bandgap semiconductor with a high concentration of itinerant defects, has  $\chi_s=+10 \times 10^{-6}$  emu/mol at 300 K [14].

The magnetic behaviour of  $Cu[Ti_2]S_4$  itself is similar to that reported by Le Nagard *et al.* 

[9]; they obtained  $\chi_m$ =+500 × 10<sup>-6</sup> emu/mol at 300 K with a weakly paramagnetic temperature dependence and ascribed this to Pauli paramagnetism, implying an unusually high electronic density of states at the Fermi level. However, the observed temperature dependence cannot be accounted for by Pauli paramagnetism. Furthermore, the high measured magnetic susceptibility of Cu[Ti<sub>2</sub>]S<sub>4</sub> is inconsistent with the measured susceptibilities of the Cu<sub>1-x</sub>[Ti<sub>2</sub>]S<sub>4</sub> phases and with the reported susceptibilities of comparable compounds such as LiTiS<sub>2</sub> [15] and VSe<sub>2</sub> [16, 17], which have  $\chi_m$ =200-300 x 10<sup>-6</sup> emu/mol at 300 K. We therefore conclude that the high and temperature-dependent paramagnetic susceptibility of Cu[Ti<sub>2</sub>]S<sub>4</sub> is due in part to a paramagnetic impurity and that this impurity is dissolved away by the iodine/acetonitrile solutions that are used to extract copper.

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# TABLE II Magnetic Susceptibilities of the Defect Thiospinels

# $Cu_{1-x}[Ti_2]S_4 \ (0 \le x \le 0.93).$

<u>T (K)</u>	<u>χ<sub>m</sub> (emu/mol x 10<sup>-6</sup>)</u>	<u>χ<sub>s</sub> (emu/mol x 10<sup>-6</sup>)</u>
80	+510	+720
112	+490	+690
163	+460	+660
210	+380	+580
293	+320	+520
77-293	+100	+290
77-293	+74	+250
77-293	+36	+200
	<u>T (K)</u> 80 112 163 210 293 77-293 77-293 77-293	$\begin{array}{c cccc} \underline{T(K)} & \underline{\chi_m (emu/mol \ x \ 10^{-6})} \\ \hline & 80 & +510 \\ 112 & +490 \\ 163 & +460 \\ 210 & +380 \\ 293 & +320 \\ 77-293 & +100 \\ 77-293 & +74 \\ 77-293 & +36 \\ \end{array}$

 $\chi_{\rm m}$  = measured molar magnetic susceptibility

 $\chi_s$  = molar susceptibility corrected for atomic diamagnetism

# TABLE III Results of the <sup>65</sup>Cu Solid-State NMR Measurements

Compound	65 <u>Cu Chemical Shift (ppm)</u>	Linewidth (kHz)
Cu[Ti <sub>2</sub> ]S <sub>4</sub>	+3035	6.05
Cu <sub>0.75</sub> [Ti <sub>2</sub> ]S <sub>4</sub>	+2171	26.6
Cu <sub>0.25</sub> [Ti <sub>2</sub> ]S <sub>4</sub>	+3654	9.9
Cu <sub>0.07</sub> [Ti <sub>2</sub> ]S <sub>4</sub>	+3831	2.2

The linewidth refers to the full width at half height of the resonance.

# $^{65}Cu NMR of Cu_{1-x}[Ti_2]S_4 (0 \le x \le 0.93)$

<sup>65</sup>Cu static NMR spectra were obtained from samples of  $Cu_{1-x}[Ti_2]S_4$  with x=0, 0.25, 0.75, and 0.93; the measured chemical shifts and linewidths of the <sup>65</sup>Cu resonances are given in Table III. In each case, the <sup>65</sup>Cu resonance exhibited a large Knight shift relative to CuCl; for comparison, the Knight shift in metallic copper is +2319 ppm. The theoretical magnitude of the Knight shift can be approximated by the following expression [18]:

$$K = \frac{\Delta B}{B_o} \sim \chi_s \frac{|\psi(0)|}{N}$$

where

The Pauli paramagnetic susceptibility.

 $|\psi(0)|^2$  = The density-of-states at the copper nuclei of electrons at the Fermi energy.

Ν

χs

= The average conduction-electron density-of-states at the Fermi energy.

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The magnetic-susceptibility data for the copper-deficient phases, presented above, show that  $\chi_s$  decreases as copper is removed; the increasing Knight shift must, therefore, be due to an increase in the Cu:4s character of the conduction electrons in the copper-deficient phases as copper is removed. The anomalously high Knight shift of Cu[Ti<sub>2</sub>]S<sub>4</sub>, like its high and temperature-dependent paramagnetic susceptibility, is consistent with an additional paramagnetic shift from an impurity paramagnetic ion. Support for this model is provided by the spin-lattice relaxation time, T<sub>1</sub>=2.2 ms, of the <sup>65</sup>Cu nuclei in Cu[Ti<sub>2</sub>]S<sub>4</sub>; this value of T<sub>1</sub> is significantly longer than that expected on the basis of the Korringa relationship [22] for relaxation due to interaction with the conduction electrons, implying that the true conduction-electron density at the copper nuclei may be lower than that implied by the observed Knight shift.

The large increase in linewidth on going from  $Cu[Ti_2]S_4$  to  $Cu_{0.75}[Ti_2]S_4$  reflects the appearance of an electric-field gradient at the <sup>65</sup>Cu nuclei due to removal of neighbouring copper atoms. A quadrupole-coupling constant of the order of 5 MHz would give a second-order quadrupole interaction large enough to account for the increase in the linewidth. On removing more copper from  $Cu_{0.75}[Ti_2]S_4$  the <sup>65</sup>Cu linewidth decreases again; at the limiting composition  $Cu_{0.07}[Ti_2]S_4$  the Cu-Cu dipolar interactions are negligible, and hence the narrow resonance implies that the site symmetry of the copper atoms is very close to the ideal, cubic crystallographic site symmetry. The residual linewidth is partly due to weak Cu-Ti dipolar coupling, but arises primarily from the second-order quadrupolar interactions caused by the small, random distortions of the [Ti\_2]S\_4 framework in  $Cu_{0.07}[Ti_2]S_4$ .



Lithium Composition, x



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Open-circuit Voltage Measurements.

The open-circuit voltages (OCV's) of  $\text{Li}_x \text{Cu}[\text{Ti}_2]S_4$  (0<x<0.5) and  $\text{Li}_x \text{Cu}_{0.07}[\text{Ti}_2]S_4$  (0<x<2) versus lithium metal as a function of lithium composition are given in figure 4. The smooth decrease in the OCV's of both compounds with increasing lithium content implies that the lithiated materials are single phase throughout the composition range studied; this was confirmed by X-ray diffraction of the electrochemically lithiated phases. The OCV of  $\text{Li}_x \text{Cu}_{0.07}[\text{Ti}_2]S_4$  is approximately 100 mV higher than that of the corresponding layered titanium disulfide  $\text{Li}_x \text{Ti}S_2$  (0<x<1) over the whole lithium-composition range; the absence of any discontinuity at the normal spinel composition  $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]S_4$  suggests that the inserted lithium occupies the 16c-octahedral sites of the thiospinel framework even at low lithium compositions.

An interesting feature of the OCV measurements is that the presence of copper results in a higher OCV ( $x \le 0.5$ ) for the lithiated normal thiospinel Li<sub>x</sub>Cu[Ti<sub>2</sub>]S<sub>4</sub> than for Li<sub>x</sub>Cu<sub>0.07</sub>[Ti<sub>2</sub>]S<sub>4</sub>. A similar phenomenon has been observed in the corresponding zirconium compounds Li<sub>x</sub>Cu[Zr<sub>2</sub>]S<sub>4</sub> and Li<sub>x</sub>Cu<sub>0.05</sub>[Zr<sub>2</sub>]S<sub>4</sub> [8].

# **Discussion**

The experimental results presented above can be explained by considering the semiempirical band diagrams of  $Cu[Ti_2]S_4$  and  $Cu_{0.07}[Ti_2]S_4$  in figure 5. Construction of these diagrams is based on the following reasoning: the Cu-S interactions are expected to be similar to those found in  $Cu_2S$ ; the Ti-S and Ti-Ti interactions to be similar to those in TiS<sub>2</sub>. To these interactions must be added the Cu-S-Ti interactions in the thiospinels.



FIG. 5: Semi-empirical band diagrams of Cu[Ti<sub>2</sub>]S<sub>4</sub> and Cu<sub>0.07</sub>[Ti<sub>2</sub>]S<sub>4</sub>.

In Cu<sub>2</sub>S, the Cu<sub>2</sub>s and S<sub>2</sub>p orbitals interact to form empty, antibonding conduction bands of primarily Cu<sub>2</sub>s character and filled, bonding valence bands of primarily S<sub>2</sub>p character. The filled Cu<sub>2</sub>d<sup>10</sup> manifold has its energy below the center of the S<sub>2</sub>p bands, so hybridization of the

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Cu: $3d^{10}$  and S:3p orbitals broadens the valence bands, but leaves the top of these bands of primarily S:3p character. Because hybridization pushes down the  $3d^{10}$  manifold, simple copper (II) sulfides are unknown. The broadening of the valence band by this hybridization is not sufficient to eliminate a finite energy gap between the conduction and valence bands; Cu<sub>2</sub>S is known to be a semiconductor with an intrinsic energy gap of 0.5-1.0 eV.

In layered  $TiS_2$ , the bottom of the titanium 3d bands lies close to the top of the valence band, which is primarily sulfide-3p in character; it is well known, for example, that heating layered  $TiS_2$  results in a reversible, partial oxidation of sulfide to sulfur by  $Ti^{4+}$ , and it proved nontrivial to prove that stoichiometric  $TiS_2$  is a small-bandgap (~0.3 eV) semiconductor rather than a semimetal [19,20]. A similar situation can be expected to prevail in the hypothetical cubic titanium disulfide c-[Ti<sub>2</sub>]S<sub>4</sub> prepared by total extraction of copper from Cu[Ti<sub>2</sub>]S<sub>4</sub>, although the thermodynamic instability of such a material relative to layered  $TiS_2$  implies an even smaller bandgap between bonding and antibonding states in the cubic disulfide.

In Cu[Ti<sub>2</sub>]S<sub>4</sub> itself, the interaction of the Cu:4s orbitals with the primarily S:3p valence band of the [Ti<sub>2</sub>]S<sub>4</sub> framework lowers the energy of the valence band relative to that in TiS<sub>2</sub> and raises that of the Cu:4s band so that it overlaps the Ti:3d conduction band. Moreover, the Cu:4s-S-Ti:3d interactions are strong, giving rise to a broadened and hybridized conduction band in Cu[Ti<sub>2</sub>]S<sub>4</sub> that overlaps the valence band in this material.

Oxidative extraction of copper from  $Cu[Ti_2]S_4$  progressively eliminates the Cu:4s-Ti:3d hybridization of the conduction bands and therefore reduces the density of states at the bottom of the conduction band; it also lowers the conduction-electron density. As long as the Fermi energy,  $E_f$ , lies above the top of the valence band (i.e. the density of overlapping states remains less than the density of copper atoms), then chemical extraction of the copper need not compete with oxidation of sulfide ions. However, it appears that  $E_f$  drops into the valence band at a critical copper concentration  $Cu_{0.07}[Ti_2]S_4$ . At this composition, the S:3p character of the electrons at the Fermi energy is sufficient to make oxidation of sulfide ions to sulfur the preferred oxidative process.

The  $^{65}$ Cu NMR data for the Cu<sub>1-x</sub>[Ti<sub>2</sub>]S<sub>4</sub> phases, which imply that the conduction electrons at the Fermi energy have substantial Cu:4s character in all of the samples, are consistent with the semiempirical band model presented above. The increase in the  $^{65}$ Cu Knight shift as copper is extracted implies that the Cu:4s character is greatest at the bottom of the conduction band.

Finally, since the conduction band in  $Cu[Ti_2]S_4$  is only one-sixth filled, the broadening of the conduction band by Cu:4s-S-Ti:3d interactions will result in a lowering of the Fermi energy in this material relative to that in  $Cu_{0.07}[Ti_2]S_4$ . This effect is clearly shown by the observation that the open-circuit voltage (i.e. the negative free energy) for lithium insertion into  $Cu[Ti_2]S_4$  is higher than that for lithium insertion into  $Cu_{0.07}[Ti_2]S_4$ ; since the electrostatic site potential of the inserted lithium is expected to be higher for the normal spinel because of electrostatic repulsion from copper atoms in face-sharing 8a sites, the greater OCV for lithium insertion into  $Cu[Ti_2]S_4$  must be due to the higher electronic work function in this material that results from conduction-band broadening.

# **Conclusions**

Characterization of the defect thiospinels  $Cu_{1-x}[Ti_2]S_4$ ,  $0 < x \le 0.93$  has led to the following conclusions:

(1) The limiting composition  $Cu_{0.07}[Ti_2]S_4$  obtained by oxidative extraction of copper from  $Cu[Ti_2]S_4$  is not determined by structural considerations; it is imposed by an oxidation of the sulfide-ion array that occurs because of an overlap of the conduction and valence bands. For

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x>0.93, the Fermi energy penetrates the valence band, thereby introducing holes into the S<sup>2</sup>-:3p<sup>6</sup> band that become trapped out in S-S bonds.

(2) Hybridization of the Cu-4s and Ti-3d bands is exceptionally strong; it results from the relative positions of Cu and Ti in the periodic table as well as the stronger Madelung potential at the titanium sites. The strong hybridization of Cu-4s and Ti-3d bands broadens the conduction band to where it overlaps the S<sup>2</sup>:3p<sup>6</sup> valence band, it introduces the strong Cu-4s character at the Fermi energy near the bottom of the conduction band that is reflected in the remarkable Knight shift of the <sup>65</sup>Cu NMR resonance, and it makes the OCV of Li<sub>8</sub>Cu[Ti<sub>2</sub>]S<sub>4</sub> higher than that of Li<sub>8</sub>Cu<sub>0.07</sub>[Ti<sub>2</sub>]S<sub>4</sub> despite the larger number of electrons in the conduction band of the former.

(3) The conduction-band electrons are itinerant, but an unidentified magnetic impurity present in  $Cu[Ti_2]S_4$  appears to be dissolved by acetonitrile during copper extraction.

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