

spectrum and as  $\text{Cl}_2$  (1.2 mmol) by color and molecular weight. Unreacted  $\text{CF}_3\text{SF}_4\text{Cl}$  was also recovered.

**Reaction of  $\text{CF}_3\text{SF}_4\text{Cl}$  with  $\text{NOCl}$ .** A 50-ml Pyrex glass vessel which contained equimolar amounts (1.5 mmol) of  $\text{CF}_3\text{SF}_4\text{Cl}$  and  $\text{NOCl}$  was heated at  $150^\circ$  for 12 hr. After separation,  $\text{CF}_3\text{NO}$ ,  $\text{SiF}_4$ , and unreacted  $\text{CF}_3\text{SF}_4\text{Cl}$  were identified by using infrared. Chlorine was also found. The yield of  $\text{CF}_3\text{NO}$  was 40%. Similar products were found after uv irradiation of the reaction mixture in a quartz vessel.

**Preparation of  $\text{CF}_3\text{SF}_4\text{SF}_4\text{CF}_3$ .** A 2:1 mmol mixture of  $\text{CF}_3\text{SF}_4\text{Cl}$  and hydrogen in a 300-ml Pyrex vessel was photolyzed by using a Hanovia Utility model uv lamp for 10 hr. After trap-to-trap fractionation, a 50% yield of  $\text{CF}_3\text{SF}_4\text{SF}_4\text{CF}_3$  was found in a trap cooled to  $-78^\circ$ .

**Preparation of  $\text{CF}_3\text{SF}_4\text{NC}(\text{Cl})\text{CF}_3$ .** Irradiation of a mixture of  $\text{CF}_3\text{CN}$  (6 mmol) and  $\text{CF}_3\text{SF}_4\text{Cl}$  (5 mmol) in a quartz vessel for 12 hr gave, after trap-to-trap separation and subsequent purification by using a 6-ft FS-1265 GC column,  $\text{CF}_3\text{SF}_4\text{NC}(\text{Cl})\text{CF}_3$  (2.5 mmol) and  $\text{CF}_3\text{SF}_4\text{SF}_4\text{CF}_3$  (1 mmol).

**Preparation of  $\text{CF}_3\text{SF}_4\text{NCCl}_2$ .** Using the same reaction and purification conditions as above,  $\text{CF}_3\text{SF}_4\text{Cl}$  (5 mmol) was reacted with  $\text{ClCN}$  to give  $\text{CF}_3\text{SF}_4\text{NCCl}_2$  (2.3 mmol) and  $\text{CF}_3\text{SF}_4\text{SF}_4\text{CF}_3$  (1 mmol).

**Preparation of  $\text{CF}_3\text{SF}_4\text{NCF}_3$ .** One millimole of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$  was condensed onto an excess of  $\text{CsF}$  in a 75-ml Hoke reaction vessel and was heated at  $100^\circ$  for 4 hr. Nearly quantitative conversion to  $\text{CF}_3\text{SF}_4\text{NCF}_3$  occurs.

**Preparation of  $\text{CF}_3\text{SF}_3=\text{NCF}_3$ .** When  $\text{CF}_3\text{SF}_4\text{NCCl}_2$  was condensed on excess  $\text{CsF}$  in a Hoke vessel and allowed to remain at  $25^\circ$  for 10 hr, a volatile compound identified as  $\text{CF}_3\text{SF}_3\text{NCF}_3$  in >99% yield was found.

**Preparation of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$ .** After 5 hr at  $60^\circ$ , a mixture of  $\text{CF}_3\text{SF}_3\text{NCF}_3$  (1 mmol) and  $\text{ClF}$  (1.5 mmol) reacted to form  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$  in a yield >98%. For final purification an 8-ft Kel-F column was used. When  $\text{CsF}$  is present,  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$  is formed in similar yields at  $25^\circ$ .

**Preparation of  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_3$ .** Hydrogen fluoride (2 mmol) was reacted with  $\text{CF}_3\text{SF}_3\text{NCF}_3$  (1 mmol) in a 75-ml Hoke reaction vessel at  $60^\circ$  for 5 hr. The reaction mixture was transferred into a second Hoke vessel which contained  $\text{NaF}$ . After 12 hr at  $25^\circ$ , the volatile mixture was separated by trap-to-trap distillation. Retained in a trap at  $-78^\circ$  was  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_3$  in 40% yield.

An equimolar mixture of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$  (1 mmol) and  $\text{HCl}$  was condensed into a Pyrex vessel at  $-183^\circ$  and allowed to warm slowly to  $25^\circ$ . A quantitative yield of  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_3$  was found.

**Preparation of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ .** Into a 75-ml vessel at  $-183^\circ$  which contained  $\text{CsF}$  were condensed  $\text{CF}_3\text{SF}_4\text{N}=\text{CF}_3$  (2 mmol) and  $\text{ClF}$  (3 mmol). The mixture was allowed to remain at  $25^\circ$  for 8 hr. A quantitative yield of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$  was obtained.

**Preparation of  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_2\text{CF}_3$ .** In a Pyrex vessel at  $25^\circ$ , equimolar amounts of  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$  (1 mmol) and  $\text{HCl}$  were reacted to give  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_2\text{CF}_3$  in >99% yield.

The spectral, analytical, and thermodynamic data for these new compounds are given in Tables II and Table III.

**Acknowledgment.** Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Mr. Stan Morse for mass spectra and Mr. Chit Srivanavith for nuclear magnetic resonance spectra.

**Registry No.**  $\text{CF}_3\text{SF}_4\text{Cl}$ , 25030-42-6;  $\text{CF}_3\text{SF}_4\text{SF}_4\text{CF}_3$ , 1580-11-6;  $\text{CF}_3\text{SF}_4\text{NC}(\text{Cl})\text{CF}_3$ , 56868-52-1;  $\text{CF}_3\text{SF}_4\text{NCCl}_2$ , 56868-53-2;  $\text{CF}_3\text{SF}_4\text{NCF}_3$ , 56868-55-4;  $\text{CF}_3\text{SF}_3=\text{NCF}_3$ , 56868-56-5;  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_3$ , 56868-57-6;  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_3$ , 56868-58-7;  $\text{CF}_3\text{SF}_4\text{N}(\text{Cl})\text{CF}_2\text{CF}_3$ , 56868-59-8;  $\text{CF}_3\text{SF}_4\text{N}(\text{H})\text{CF}_2\text{CF}_3$ , 56868-60-1;  $\text{ClF}$ , 7790-89-8;  $\text{CF}_3\text{SF}_3$ , 374-10-7;  $\text{NOCl}$ , 2696-92-6;  $\text{CF}_3\text{NO}$ , 334-99-6;  $\text{H}_2$ , 1333-74-0;  $\text{CF}_3\text{CN}$ , 353-85-5;  $\text{ClCN}$ , 506-77-4;  $\text{CsF}$ , 13400-13-0;  $\text{HF}$ , 7664-39-3;  $\text{HCl}$ , 7647-01-0;  $\text{CF}_3\text{SSCF}_3$ , 372-64-5.

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## Convenient Preparation and Physical Properties of Lithium Intercalation Compounds of Group 4B and 5B Layered Transition Metal Dichalcogenides

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Received March 18, 1975

AIC50199I

*n*-Butyllithium in hexane solution has been found to be a mild and efficient reagent for intercalation of lithium into the layered  $\text{MX}_2$  compounds ( $M = \text{Ti, Zr, Hf, V, Nb, Ta}$ ;  $X = \text{S, Se, Te}$ ), most of which were prepared in this study. All the compounds attained a limiting composition of  $\text{LiMX}_2$  except  $\text{VSe}_2$  which formed  $\text{Li}_2\text{VSe}_2$ . For the group 5B compounds this is more lithium than can be intercalated at high temperatures or from lithium-ammonia solutions. The tellurides, which decompose under previous reaction conditions, were intercalated using *n*-BuLi. Crystallographic, magnetic susceptibility, pressed pellet dc conductivity, and superconductivity data are reported. Only the  $\text{LiZrX}_2$  compounds were superconducting. All compounds have a low room-temperature resistivity ( $10^{-2}$ – $10^{-3}$   $\Omega$  cm in pressed powders) except  $\text{Li}_2\text{VSe}_2$  which has  $\rho_{298^\circ\text{K}} = 6 \times 10^3$   $\Omega$  cm.  $\text{Li}_2\text{VSe}_2$  contains  $\text{V}^{2+}$  having  $S = 3/2$  and  $g = 1.98$  and possible antiferromagnetic ordering below  $20^\circ\text{K}$ . Only  $\text{LiTiSe}_2$  gave any indication in magnetic susceptibility of a possible charge density wave instability similar to those observed in  $d^1$   $\text{MX}_2$  compounds.

A number of alkali metal intercalates of the groups 4B, 5B, and 6B layered transition metal dichalcogenides have been reported.<sup>1-7</sup> These compounds have been prepared either by combination of the elements at high temperature, by treating

the parent  $\text{MX}_2$  with a solution of the alkali in liquid ammonia, or by treatment with lithium naphthalide. These methods have drawbacks, particularly for lithium intercalation. High-temperature methods may lead to decomposition or only partial

intercalation. The alkali metals also attack quartz reaction tubes at high temperature. Reactions in liquid ammonia usually give products which have incorporated ammonia. Although the ammonia may usually be removed at elevated temperatures in vacuo (250°C for LiTiS<sub>2</sub><sup>7</sup>), the space taken up by the ammonia during reaction may in some cases prevent full intercalation of the alkali.<sup>8</sup> Many transition metals can also catalyze formation of LiNH<sub>2</sub> from lithium in liquid ammonia. Some physical properties of 2H-TaS<sub>2</sub> have been shown to be affected by sulfur removal in pure liquid ammonia.<sup>9</sup> Such sulfur removal may occur with alkali metal ammonia solutions and with other MX<sub>2</sub> as well. Electron transfer catalysts such as naphthalene in solvents such as THF or DME have been used, but cointercalation of solvent and/or catalyst may occur.

A procedure for preparation of these compounds under milder conditions alleviating the drawbacks of high-temperature methods and ammonia solutions would be of value in preparing pure compounds for measurement of physical properties. We report here that *n*-butyllithium (*n*-BuLi) in hexane solution is a mild reagent for the intercalation of lithium into group 4B and 5B metal dichalcogenides, free of complicating side reactions.<sup>10</sup> In addition to many previously known intercalation complexes, this method has allowed us to prepare lithium intercalation compounds of the ditellurides, which decompose under reaction conditions used previously. Surprisingly, we have also prepared Li<sub>2</sub>VSe<sub>2</sub>, the first example of such stoichiometry in these compounds.

Although a number of Li<sub>x</sub>MX<sub>2</sub> compounds have been prepared, few physical measurements (except x-ray data) have been reported, probably because of the moisture sensitivity of the compounds<sup>11</sup> and their varying stoichiometries. We have tried to fill this void with crystallographic, magnetic susceptibility, conductivity, and superconductivity data for the compounds prepared.

Of particular interest is the possibility of charge density wave (cdw) instabilities in the group 4B LiMX<sub>2</sub> since they are isoelectronic with the group 5B MX<sub>2</sub>, many of which have cdw instabilities.<sup>12-14</sup> At onset of the cdw in group 5B MX<sub>2</sub> compounds, the magnetic susceptibility usually decreases providing a possible indicator of the cdw.

### Experimental Section

All of the MX<sub>2</sub> compounds used were prepared by published procedures.<sup>15,16</sup> *n*-Butyllithium (2.4 M in hexane) was purchased from Alfa Products and was standardized periodically by titration with *n*-butyl alcohol in xylene using 1,10-phenanthroline as indicator according to the procedure of Watson and Eastham.<sup>17</sup>

All reactions were carried out under argon in dried Schlenkware. All transfers of the products, which are moisture sensitive, were made in an argon filled inert atmosphere box. In a typical reaction 3.00 ml of *n*-BuLi (7.06 mmol) was added to 0.5410 g of ZrSe<sub>2</sub> (2.17 mmol) in a Schlenk tube. The mixture rapidly became hot enough to boil the hexane and the ZrSe<sub>2</sub> (gold-brown powder) became dark green. After half an hour the mixture was heated to 60°C for 10 hr to ensure completion of the reaction. No exfoliation was observed in these reactions. The product was filtered in the Schlenk frit and washed with ether. The filtrate containing excess *n*-BuLi was titrated with 0.953 M *n*-butyl alcohol in xylene using 1,10-phenanthroline indicator. The titration required 5.15 ml of the alcohol-xylene solution, allowing calculation of the stoichiometry as Li<sub>0.99</sub>ZrSe<sub>2</sub>. We feel the stoichiometry calculations are good to ±2%.

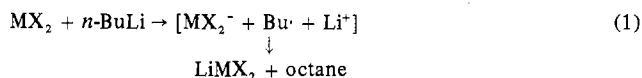
Early experiments with dilute *n*-BuLi (~0.5 M) at room temperature gave only partial intercalation. In general an excess of *n*-BuLi was used, but with VSe<sub>2</sub> this led to formation of a hexane soluble red side product (x-ray fluorescence measurements indicate it contained both V and Se). To inhibit this decomposition LiVSe<sub>2</sub> and Li<sub>2</sub>VSe<sub>2</sub> were prepared with stoichiometric amounts of *n*-BuLi. Addition of 1,10-phenanthroline indicated all the *n*-BuLi had been consumed.

Capillary tubes for Debye-Scherrer x-ray powder photographs were loaded in the glove box and sealed with wax and then with a flame outside the box. A Teflon holder with a tight-fitting top was used

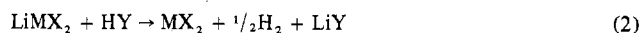
for superconducting *T<sub>c</sub>* measurements by the usual low-frequency ac susceptibility method.<sup>16</sup> Samples for magnetic susceptibility (~200 mg) were loaded in thin-wall quartz tubing inside the glove box, evacuated, back filled with 20 Torr of helium, and sealed prior to measurement using the Faraday technique previously described.<sup>18</sup> Four point conductivity measurements were made using powdered samples pressed into a Plexiglas die with brass plungers which served as the current leads. The voltage leads were 1/32 in. stainless steel screws sharpened to a point and screwed into the die to make contact. The hexagonal layered compounds have highly anisotropic conductivities,<sup>19</sup> for example 2H-NbSe<sub>2</sub>  $\rho$  parallel to the *c* axis/ $\rho$  perpendicular to the *c* axis is 30 at 300°K.<sup>20</sup> Several of the parent compounds were measured and gave  $\rho$  values within a factor of 5 of literature values for  $\rho_{\perp}$ . Since these are pressed powders, with not all the particles aligned, these higher values were not unexpected.

### Results and Discussion

The reaction to give LiMX<sub>2</sub> from *n*-BuLi and MX<sub>2</sub> is conceptually analogous to the use of electron-transfer reagents such as lithium naphthalide. Although *n*-BuLi is mainly a covalent hexamer in hexane, its chemistry is conveniently thought of as arising from Li<sup>+</sup>(*n*-Bu)<sup>-</sup>. The intercalation then is conceptually electron transfer from Bu<sup>-</sup>, the lithium ion intercalating to balance the charge. The advantage over electron-transfer reagents is that commercially available solutions in a noncoordinating solvent (hexane) may be used avoiding any solvent intercalation. Octane and LiMX<sub>2</sub> are the sole products as shown in eq 1. The formation of octane



was confirmed by gas chromatography (GLC). Besides titration of excess *n*-BuLi, measurement of octane formation by GLC is another method of determining stoichiometry. Stoichiometry was also determined for LiTaS<sub>2</sub> and LiNbSe<sub>2</sub> by addition of excess standard acid solution to LiMX<sub>2</sub> and titrating the acid consumed by the reaction in eq 2. This



method is unsatisfactory for the group 4 compounds because of varying degrees of hydrolysis of the chalcogenides to give amphoteric oxides.

The limiting composition in all cases studied except VSe<sub>2</sub> appears to be one lithium. No attempt was made to prepare less than fully intercalated compounds, except for Li<sub>2</sub>VSe<sub>2</sub>. High-temperature methods and preparations from ammonia solution generally give Li/M ≤ 0.8 for the group 5 compounds.<sup>5,8</sup> In cases where our measured stoichiometry was low (Li<sub>0.85</sub>TiSe<sub>2</sub> and 1T-Li<sub>0.82</sub>TaS<sub>2</sub>) no attempt was made to improve it. In the case of VSe<sub>2</sub> the limiting composition is Li<sub>2</sub>VSe<sub>2</sub>, which is the first example of this stoichiometry for the dichalcogenides. The existence of Li<sub>2</sub>VSe<sub>2</sub> is apparently a result of the greater stability of V<sup>2+</sup> compared to the divalent ions of the other group 4B and 5B metals. We believe that Li<sub>2</sub>VSe<sub>2</sub> is a layered compound based on maintenance of hexagonal symmetry on going from VSe<sub>2</sub> to Li<sub>2</sub>VSe<sub>2</sub> (see crystallographic results) and since the isoelectronic VCl<sub>2</sub> is also known to have the CdI<sub>2</sub> structure.<sup>21</sup> We were unable to prepare Li<sub>2</sub>VS<sub>2</sub> from the known LiVS<sub>2</sub>. In retrospect it is somewhat surprising that the Ti compounds do not form Li<sub>2</sub>MX<sub>2</sub> compounds since TiCl<sub>2</sub> also has the CdI<sub>2</sub> structure<sup>22</sup> and the empty t<sub>2g</sub> band could accommodate two electrons.

The group 4B MX<sub>2</sub> are very reactive toward *n*-BuLi, generally exothermic enough to boil the hexane solution, whereas the Nb and Ta compounds were not, even though color change of MX<sub>2</sub> from steel gray to silvery was rapid. Reaction of VSe<sub>2</sub> with *n*-BuLi was quite exothermic after a short induction period. All the LiMX<sub>2</sub> were moisture sensitive,<sup>11</sup> especially the group 4B LiMX<sub>2</sub> which were on occasion pyrophoric.

Table I. Hexagonal Unit Cell Dimensions<sup>f</sup>

Comps	<i>a</i> , Å	<i>c</i> , Å	10 <sup>6</sup> χ <sub>M</sub> (300°K), <sup>a</sup> emu/mol	ρ, Ω cm (298°K)	T <sub>c</sub> , °K
1T-Li <sub>1.0</sub> TiS <sub>2</sub>	3.423 (3.405)	6.222 (5.690)	177	1.4 × 10 <sup>-3</sup> (5 × 10 <sup>-3</sup> )	<0.5
1T-Li <sub>0.85</sub> TiSe <sub>2</sub>	3.643 (3.535)	6.431 (6.004)	246		<0.5
3s-Li <sub>1.0</sub> ZrS <sub>2</sub> <sup>b</sup>	3.672 (3.662)	3 × 6.306 (5.813)	16 <sup>c</sup>	6.8 × 10 <sup>-3</sup> (1)	1.94-1.0
1T-Li <sub>0.99</sub> ZrSe <sub>2</sub>	3.732 (3.770)	6.637 (6.138)	13 <sup>c</sup>	8.7 × 10 <sup>-3</sup>	1.05-0.5
1T-Li <sub>0.95</sub> ZrTe <sub>2</sub>	4.014 (3.950)	6.942 (6.630)	-14 <sup>c</sup>	7.4 × 10 <sup>-2</sup>	0.67-<0.5
1T-Li <sub>0.97</sub> HfS <sub>2</sub>	3.548 (3.635)	6.344 (5.837)	-7	9.5 × 10 <sup>-3</sup> (>10 <sup>5</sup> )	<0.5
1T-Li <sub>0.96</sub> HfTe <sub>2</sub>	3.992 (3.949)	7.092 (6.651)			
1T-Li <sub>1.0</sub> VSe <sub>2</sub>	3.58 (3.35)	6.40 (6.10)	815	4.2 × 10 <sup>-2</sup> (9 × 10 <sup>-4</sup> )	<0.5
1T-Li <sub>1.0</sub> VSe <sub>2</sub>	4.01	6.45	<i>d</i>	6 × 10 <sup>3</sup>	
2H-Li <sub>1.06</sub> NbSe <sub>2</sub>	3.502 (3.45)	2 × 6.80 (2 × 6.27)		1.35 × 10 <sup>-3</sup> (4 × 10 <sup>-4</sup> )	
Li <sub>0.92</sub> NbTe <sub>2</sub> <sup>e</sup>	3.75 (3.75)	7.00 (6.68)		2.72 × 10 <sup>-3</sup>	
2H-Li <sub>0.99</sub> TaS <sub>2</sub>	3.314 (3.315)	2 × 6.392 (2 × 6.05)	-44	7.0 × 10 <sup>-4</sup>	
1T-Li <sub>0.82</sub> TaS <sub>2</sub>	3.343 (3.346)	6.461 (5.860)			
2H-Li <sub>0.99</sub> TaSe <sub>2</sub>	3.449 (3.434)	2 × 6.801 (2 × 6.348)		7.6 × 10 <sup>-2</sup> (4.0 × 10 <sup>-4</sup> )	
Li <sub>0.94</sub> TaTe <sub>2</sub> <sup>e</sup>	3.75 (3.74)	7.10 (6.72)		8.2 × 10 <sup>-3</sup>	
Pd			550		
V <sub>3</sub> Si			407 (per V)		

<sup>a</sup> Corrected for paramagnetic impurities but not core diamagnetism; see text for details. <sup>b</sup> Parent compound used was 1T-ZrS<sub>2</sub>. <sup>c</sup> Values uncorrected for paramagnetic impurities. <sup>d</sup> Antiferromagnetic; see text. <sup>e</sup> Parent compound is monoclinic; values given are pseudo-hexagonal. <sup>f</sup> Values in parentheses are for parent MX<sub>2</sub>.

Table II. Crystallographic Data for Li<sub>2</sub>VSe<sub>2</sub>

<i>d</i> (obsd)	<i>d</i> (calcd)	<i>l</i>	( <i>hkl</i> )
6.50	6.450	m	001
3.45	3.473	w	100
3.22	3.225	w	002
3.07	3.058	s	101
2.37	2.363	m <sup>+</sup>	102
2.02	2.005	s	110
1.92	1.915	w	111
1.83	1.828	w	103
1.70	1.736		200
	1.703	w <sup>+</sup>	112
1.68	1.677		201
1.61	1.613	w <sup>+</sup>	004
1.535	1.529	w	202
	1.466		113
1.46	1.463	w	104
1.355	1.351	w	203
1.29	1.290		005
	1.286	w	211
1.26	1.256	w	114
	1.216		212
1.22	1.209	w	105

### Crystallographic Results

All compounds gave sharp x-ray powder patterns. The data were refined by least squares to give the hexagonal *a* and *c* parameters shown in Table I. The data for the new compound Li<sub>2</sub>VSe<sub>2</sub> are given in Table II. The interlayer spacing (*c* for 1T, *c*/2 for 2H, *c*/3 for 3s) increases by 0.30–0.60 Å following intercalation, while the *a* axis generally increases or decreases by less than 0.1 Å, except for VSe<sub>2</sub>. The x-ray data of the group 4B LiMX<sub>2</sub> agree well with those obtained from compounds prepared from ammonia solution.<sup>7</sup> The group 5B LiMX<sub>2</sub> are of higher stoichiometry than when prepared by other methods and the crystallographic data<sup>5</sup> cannot be readily compared.

The maintenance of hexagonal symmetry in Li<sub>2</sub>VSe<sub>2</sub> and the similarity in intensities of corresponding *d* spacings to those of VSe<sub>2</sub>, especially of the (001), (101), (102), and (110) reflections, strongly suggest that Li<sub>2</sub>VSe<sub>2</sub> has a similar structure. The dramatic change in *a* for VSe<sub>2</sub> (3.35 Å) going to LiVSe<sub>2</sub> (3.58 Å) and finally to Li<sub>2</sub>VSe<sub>2</sub> (4.006 Å) may be attributed to the increased size of V<sup>3+</sup> and V<sup>2+</sup>, and perhaps to increased size of Se<sup>2-</sup> due to increased ionic character of the compound. The location of Li ions in Li<sub>2</sub>VSe<sub>2</sub> is of interest. In LiVS<sub>2</sub> and LiCrS<sub>2</sub>, where atomic positions of LiMX<sub>2</sub> are known, lithium occupies octahedral sites (one per M) between the layers.<sup>23</sup> Since there is only one octahedral site per V, at

least one and probably both Li occupy tetrahedral sites (two per V), this is not unreasonable since the energy difference between octahedral and tetrahedral sites is likely quite small since Li is mobile within the layer lattice (reaction occurs readily at room temperature) and must pass through a tetrahedral site to pass from one octahedral site to another.<sup>10b</sup>

The retention of the large *a* axis in 1T-Li<sub>0.85</sub>TaS<sub>2</sub> along with a single layer *c* axis repeat suggests that the Ta atoms remain octahedrally coordinated as in 1T-TaS<sub>2</sub>. The 2H compounds of group 5B remained 2H on lithiation as noted by Whittingham.<sup>10b</sup>

The monoclinically distorted NbTe<sub>2</sub> and TaTe<sub>2</sub> remain distorted after lithium intercalation.

### Conductivity

Four probe dc conductivity measurements on pressed powder pellets were made in an argon atmosphere at 298°K. The data are summarized in Table I. The poorly conducting Zr and HfX<sub>2</sub> compounds become good conductors on intercalation as expected from band models.<sup>24</sup> The room-temperature conductivities of the semimetallic TiS<sub>2</sub><sup>25</sup> and the metallic group 5B compounds do not change much on intercalation to near one lithium, showing that the room-temperature conductivity in these cases is not a sensitive function of band filling. The group 5B intercalated compounds should approach the conductivity of the group 6B MX<sub>2</sub>. The high conductivity observed is likely due to a slight deficiency from full stoichiometry and band filling (compare to 2H-W<sub>0.97</sub>Ta<sub>0.03</sub>Se<sub>2</sub> where ρ = 3 × 10<sup>-3</sup> ohm cm<sup>24</sup>). A dramatic drop in the room temperature conductivity in Li<sub>2</sub>VSe<sub>2</sub> compared to VSe<sub>2</sub> is observed, apparently due to localization of the 3d electrons (see magnetic measurements).

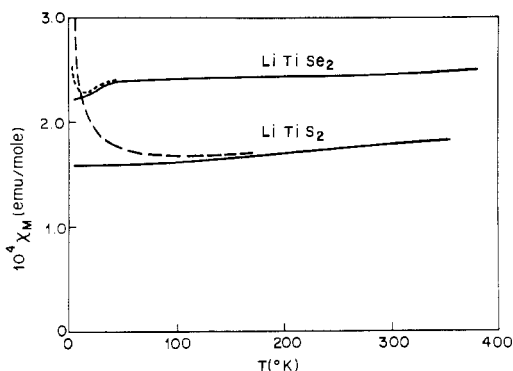
### Magnetic Measurements

Magnetic susceptibility data for many of the LiMX<sub>2</sub> prepared were obtained from room temperature to 4.2°K. The χ<sub>M</sub> values at 300°K are given in Table I after correction (where possible) for paramagnetic impurities. Detailed data for several compounds are shown in Figures 1–4.

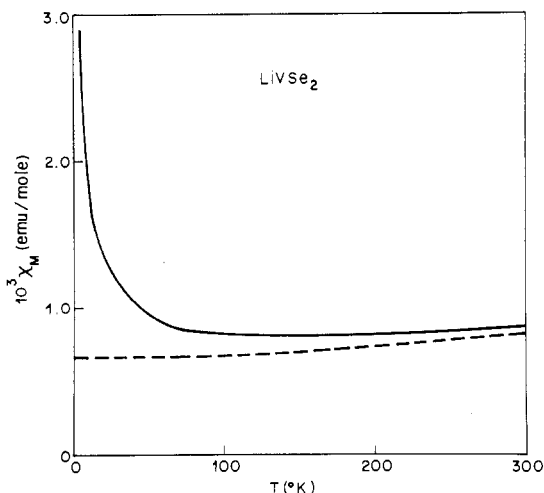
For these compounds we expect that

$$\chi_M = \chi_d + \chi_p + C/T$$

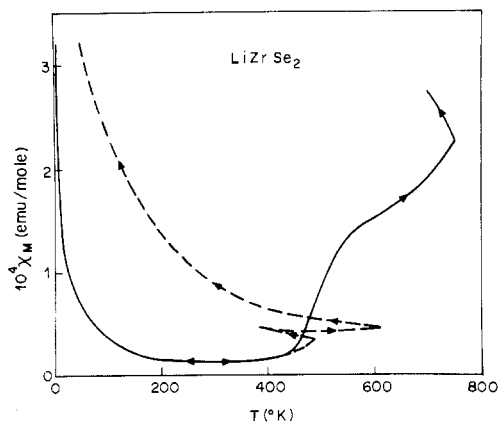
where χ<sub>d</sub> = the temperature-independent term equal to the sum of the core diamagnetism and the Van Vleck band paramagnetism; χ<sub>p</sub> = the Pauli paramagnetism of conduction electrons, which may be somewhat temperature dependent as in 2H-TaS<sub>2</sub>,<sup>13,22</sup> and C is proportional to the moment, μ<sub>eff</sub><sup>2</sup>,



**Figure 1.** The molar magnetic susceptibility from 4.2°K to near 400°K is shown for LiTiS<sub>2</sub> and LiTiSe<sub>2</sub>. The broken lines represent the data as obtained, the solid line has been corrected for paramagnetic impurities as explained in the text.



**Figure 2.** The molar magnetic susceptibility of LiVSe<sub>2</sub> as measured (—) and approximately corrected for paramagnetic impurities (---); see text.

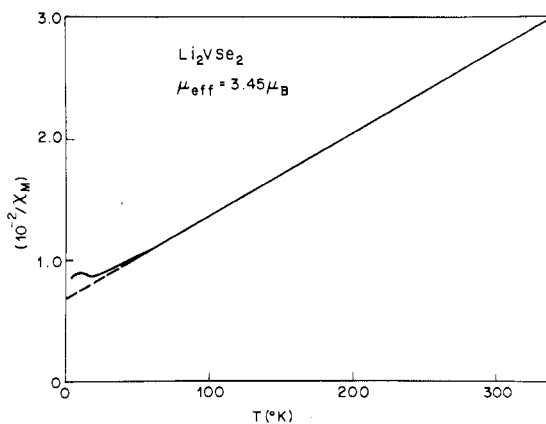


**Figure 3.** The molar magnetic susceptibility of LiZrSe<sub>2</sub> to 750°K. At low temperatures  $\chi_M$  increases due to paramagnetic impurities. Above 400°K irreversible effects occur probably due to decomposition. Two different samples are shown above 400°K.

on impurity atoms (in simple cases temperature independent); let  $\chi_i$  = intrinsic susceptibility =  $\chi_d + \chi_p$ .

All the compounds showed evidence of paramagnetic impurities, either iron (present in starting metals at 10–100 ppm) or possibly in some cases a small amount of a second phase with localized moments.

Data for LiTiS<sub>2</sub> and LiTiSe<sub>2</sub> are shown in Figure 1. The broken lines indicate raw data, while the solid line represents the data corrected for the impurity term,  $C/T$  ( $C$  is tem-



**Figure 4.** The inverse susceptibility of Li<sub>2</sub>VSe<sub>2</sub> vs.  $T$ . From these data we find  $\theta = -93^\circ\text{K}$ ,  $\mu_{\text{eff}} = 3.45 \mu_B$ , and probable anti-ferromagnetic order near 20°K.

perature independent for these compounds). In LiVSe<sub>2</sub> (Figure 2)  $C$  decreases smoothly with  $T$  (below 20°K), so that at 4.2°K  $C$  is only 30% of that at 30°K. This decrease may come from Kondo compensation of the impurity in the host moment at low temperatures.<sup>27</sup> Consequently a simple subtraction of the impurity effects is difficult. In this case, however, using  $C$  obtained between 20 and 60°K, it is found that  $\chi_i$  is constant over that temperature range. If we assume that  $\chi_i$  can be extrapolated to below 20°K,  $\chi_i$  would be given by the dashed line in Figure 2. The susceptibility for LiZrS<sub>2</sub>/Se<sub>2</sub>/Te<sub>2</sub> below 100°K cannot be fit with a constant  $C$  value. Since  $C$  is temperature dependent over such a large interval, the effects of the impurities cannot be adequately subtracted and the data as obtained for LiZrSe<sub>2</sub> are shown in Figure 3.

The magnetic susceptibility of the group 4B LiMX<sub>2</sub> is consistent with metallic behavior ( $\chi_p > 0$ ). The susceptibility is more indicative of band filling than conductivity as shown by the diamagnetism of 2H-LiTaS<sub>2</sub> (compare to semiconducting 2H-MoS<sub>2</sub>,  $\chi = -58 \times 10^{-6}$  emu/mol<sup>28</sup>) even though conductivity remained relatively high (see Table I). The measured susceptibility of LiTiS<sub>2</sub> at 295°K is approximately 35% larger than that reported<sup>29</sup> for LiTiS<sub>2</sub> prepared from ammonia solution. The susceptibilities of these compounds are expected to be anisotropic and it is not certain in either measurement that the randomly oriented value is obtained.

The most surprising compound prepared is Li<sub>2</sub>VSe<sub>2</sub>, magnetic data for which are given in Figure 4.  $\chi_M$  is described by  $\chi_M = N_0 \mu_{\text{eff}}^2 / T + \theta$  when  $T \geq 50^\circ\text{K}$ , with  $\mu_{\text{eff}} = 3.45 \mu_B$  per V and  $\theta = 93^\circ\text{K}$ . The compound appears to order antiferromagnetically near 20°K. The  $\mu_{\text{eff}}$  is somewhat less than the ideal value of 3.87  $\mu_B$  for a localized  $S = 3/2$ ,  $g = 2$  state. This may be due to some LiVSe<sub>2</sub> or some decomposition product (see Experimental Section). EPR measurements at room temperature showed a strong, broad (206 G) resonance at 3343 G with  $g = 1.9804$ , indicative of  $S = 3/2$ . The confirmation of V<sup>2+</sup> is a striking illustration of charge transfer. The isoelectronic VCl<sub>2</sub> is antiferromagnetic.

Table I also gives  $\chi_M$  for Pd (exchange enhanced) and V<sub>3</sub>Si (high density of states) for comparison to the LiMX<sub>2</sub>. The very large  $\chi_M$  of Li<sub>2</sub>VSe<sub>2</sub> is due to local moment formation, while  $\chi_M$  ( $8.15 \times 10^{-4}$  emu/mol) for LiVSe<sub>2</sub> is so large that it is  $1/4$  of the  $\chi$  expected at 300°K if the electrons were localized on V with  $S = 1$  and  $g = 2$ ! LiVSe<sub>2</sub> is, then, likely a highly exchange enhanced metal like Pd, since the calculated density of states of similar 1T compounds<sup>24</sup> would not account for the large value of  $\chi_M$ . The relatively large values of  $\chi_M$  for LiTiS<sub>2</sub> and LiTiSe<sub>2</sub> may not be inconsistent with a high density of states, but these values are also likely enhanced.

Of the LiMX<sub>2</sub> investigated only LiTiSe<sub>2</sub> showed any clear

anomaly in  $\chi_M$  ( $\approx 40^\circ\text{K}$ ) which might be associated with cdw onset. The group 5B 1T-VSe<sub>2</sub> and 1T-TaSe<sub>2</sub> have cdw onset between  $\sim 108^\circ\text{K}$  (VSe<sub>2</sub>)<sup>30</sup> and  $600^\circ\text{K}$  (1T-TaSe<sub>2</sub>)<sup>31</sup> with readily observable changes in  $\chi_M$  at or below onset. It may be that the effect of a cdw is too weak to be seen by magnetic susceptibility (as is the case with 2H-NbSe<sub>2</sub>) in all but LiTiSe<sub>2</sub>, or perhaps the instabilities occur above room temperature. Attempts to measure susceptibility in LiZrSe<sub>2</sub> (Figure 3) at high temperatures gave irreversible changes above  $400^\circ\text{K}$ . Two batches were measured giving similar results. Although x-ray powder patterns of LiZrSe<sub>2</sub> were identical before and after heating, less than 1% of an impurity phase could produce these effects in  $\chi$ . Onset of cdw above the decomposition temperature could account for the low susceptibility of LiZrSe<sub>2</sub> compared to LiTiSe<sub>2</sub>. Also possible is a spin density wave instability as in Cr metal,<sup>32,33</sup> most probable in the 3d compounds. Only further measurements will determine the correct state of affairs (including, of course, no instability at all). The most obvious experiments include NMR and electron microscopy.

### Superconductivity

Of the LiMX<sub>2</sub> we have prepared, only the Zr compounds were superconducting as determined by ac susceptibility measurements (see Table I). In compounds made from ammonia solution Revelli<sup>8</sup> observed two  $T_c$ 's of 2.56 and  $2.15^\circ\text{K}$  for Li<sub>0.8</sub>ZrS<sub>2</sub> and 0.88 and  $0.56^\circ\text{K}$  for Li<sub>0.8</sub>HfSe<sub>2</sub> and single transitions for Li<sub>0.8</sub>ZrSe<sub>2</sub> at  $1.4^\circ\text{K}$  and Li<sub>0.8</sub>HfS<sub>2</sub> at  $1.88^\circ\text{K}$ . These multiphase transitions may result from chalcogen loss on intercalation from ammonia as pointed out by Thompson.<sup>9</sup> The relationship of cdw instabilities and superconductivity which is important for the group 5B MX<sub>2</sub><sup>34</sup> is not clear in the group 4B LiMX<sub>2</sub>.

### Conclusion

In summary the use of *n*-BuLi in hexane solution provides a mild method, free of side reactions, for preparing lithium intercalation compounds of the group 4B and 5B transition metal dichalcogenides, including those of tellurides. Physical properties are consistent with those of the same compounds prepared by other methods, although properties highly sensitive to stoichiometry, such as superconductivity, are not identical. The group 5B LiMX<sub>2</sub> were prepared with one lithium per transition metal, whereas other methods have yielded lower ratios.

The properties of Li<sub>2</sub>VSe<sub>2</sub> are consistent with a layered structure with Li<sup>+</sup> occupying tetrahedral sites between layers of VSe<sub>2</sub> containing V<sup>2+</sup> with localized charges which couple antiferromagnetically at low temperature.

Although we expected the electronic properties of the group 4B LiMX<sub>2</sub> to be similar to the 5B MX<sub>2</sub> compounds which show cdw instabilities, only LiTiSe<sub>2</sub> showed any indication in the magnetic susceptibility of this instability.

Besides preparation of LiMX<sub>2</sub>, this method has allowed us to prepare compounds of the formula Li<sub>3</sub>MX<sub>3</sub> for the group

4B and 5B transition metal chalcogenides, which will be described in a forthcoming paper.

**Acknowledgment.** The authors are indebted to R. S. Hutton for the EPR measurements on Li<sub>2</sub>VSe<sub>2</sub> and helpful discussions with our colleague J. A. Wilson.

**Registry No.** LiTiS<sub>2</sub>, 55326-82-4; LiTiSe<sub>2</sub>, 55964-32-4; LiZrS<sub>2</sub>, 55964-34-6; LiZrSe<sub>2</sub>, 55964-30-2; LiZrTe<sub>2</sub>, 57014-86-5; LiHfS<sub>2</sub>, 55964-04-0; LiHfTe<sub>2</sub>, 57014-89-8; LiVSe<sub>2</sub>, 55964-31-3; Li<sub>2</sub>VSe<sub>2</sub>, 57014-85-4; LiNbSe<sub>2</sub>, 55964-36-8; LiNbTe<sub>2</sub>, 57014-88-7; LiTaSe<sub>2</sub>, 55964-35-7; LiTaTe<sub>2</sub>, 55964-33-5; LiTaTe<sub>2</sub>, 57014-87-6; ZrSe<sub>2</sub>, 12166-47-1; *n*-BuLi, 109-72-8.

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