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Stoichiometry and Physical Properties of Ternary Molybdenum Chalcogenides $M_xMo_6X_8$ (X = S, Se; M = Li, Sn, Pb)

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Chemical and electrochemical insertion of Li at room temperature, as well as insertion of lead and tin at moderate temperatures (500°C), into the binary phase Mo_6X_8 forms ternary molybdenum chalcogenides $M_xMo_6X_8$ (X = S, Se). Crystallographic parameters, superconducting properties, and magnetic susceptibility are reported. The stoichiometry x for lead and tin is shown not to exceed $x = 1$, while for Li, x can reach approximately 4.0. For the lead and tin sulfide series, the hexagonal lattice parameters and superconducting critical temperatures (T_c) are invariant to changes in the *nominal* composition of $0.8 < x < 1.2$, while both an increase in T_c and a small decrease in c_h is observed for the selenides; a narrow homogeneity range exists near $x = 1$ below 500°C for both these sulfides and selenides, the single-phase region being somewhat larger in the selenides. In contrast, several single-phase regions and large unit cell changes are observed in $Li_xMo_6X_8$ ($0 < x < 3.2$). Magnetic susceptibility measurements of the lithiated compounds at $x \sim 3.2$ reveals a structural phase transition at 140 and 185 K for the sulfide and selenide, respectively; but neither superconducts down to 1.5 K. At lower lithium concentration near $x \sim 1.0$, the T_c of the sulfide is raised from that of Mo_6S_8 (1.8 K) to 5.2 K but the T_c of Mo_6Se_8 (6.5 K) is depressed to 3.9 K.

Introduction

The class of ternary molybdenum chalcogenides of formula $M_xMo_6X_8$ (M = Pb, Sn, . . . ; X = S, Se, Te) has prompted a significant amount of experimental and theoretical work in an attempt to understand their remarkable superconducting properties. The upper critical field reaches values beyond 60T (*1*) and the critical temperature, T_c, can be as high as 15 K (*2*). Unfortunately these materials are almost never prepared as a pure single phase and there are numerous differences in the literature arising from an inability to control stoichiometry. Not only is the reported content of the ternary element M variable, but also the reported ratio of molybdenum to chalcogen is often greater than the "ideal" value 6/8.

The reported homogeneity range x of the ternary element (M) varies considerably from one system to another and is generally smaller for the selenides than for the sulfides (*3*). When M is a small cation (e.g., Cu), x may vary continuously up to 4, the small atoms being distributed over two sets of six tetrahedral sites off the crystallographic $\bar{3}$ axis (*4*). For large atoms (rare earths, Pb, Sn, etc.) M sits on the $\bar{3}$ axis and x is on the order of one. In the rare earth

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(*RE*) sequence $REMo_6S_8$ it has been reported, for example, that the composition is close to $RE_{1.0}Mo_6S_8$ for the light rare earths but for the heavy rare earths it is closer to $RE_{1.2}Mo_6S_8$ (*5*). The lead or tin sulfide compounds have been intensively investigated and both nonstoichiometry in the ternary element and changes in Mo/S ratio have been reported by Hauck (*6*) and Wagner (*7*), respectively, leading to various formulas $Pb_xMo_6S_{8-y}$ ($0.85 < x < 1.05$; $0.8 < y < 1.2$) and $Sn_xMo_{6+z}S_8$ ($0.9 < x < 1.1$; $0.2 < z < 1$). The reported x, y, and z values depend strongly on the particulars of sample preparation. This uncertainty of composition makes comparisons of different published works difficult.

The superconducting properties of these compounds result from the overlap of the 4*d* orbitals of the Mo atoms which form the doubly degenerate E_g conduction band (*8*). The width and the degree of band filling is governed by the inter- and intracluster Mo–Mo distances which are very sensitive to the size and the nature of the ternary element as well as to metal, chalcogen, or molybdenum vacancies. As a result of this sensitivity the superconducting critical temperatures reported in the literature for "$PbMo_6S_8$" range from 9 to 15 K. Because of the difficulty in sample preparation, it is still uncertain how each of the nonstoichiometric variables affect T_c. Both Sergent *et al.* (*9*) and Wagner and Freyhardt (*7*) reported that the highest T_c is obtained with excess lead and tin, respectively where as Hauck (*6*) and Delk and Sienko (*10*) observed an increase in T_c correlated to an increase in the crystallographic c_h/a_h ratio in these same systems when the nominal stoichiometry has a deficiency in chalcogen. However, recent studies by D. H. Kinks *et al.* have shown that the scattering of T_c values in the literature for these compounds may be due to the presence of oxygen defects. Again these differences come from the fact that the high-temperature technique (1200°C) used in the preparation of these materials does not easily allow separate control of the nonstoichiometric variables.

Recently the low-temperature diffusion method allowed us to prepare new Chevrel phases (*12*) with different ternary elements without affecting the Mo/S ratio. We show that this new synthetic route can be extended to the preparation of many of the known Chevrel phases, and that the nonstoichiometry in the ternary element of $M_xMo_6S_8$ compounds can be directly correlated with their structural and superconducting behavior. For this purpose the systems $M_xMo_6X_8$; M = Pb, Sn, Li; X = S, Se, have been investigated.

Experimental

The ternary lead and tin compounds were produced by reacting appropriate amounts of the pure binary phase Mo_6X_8 prepared by oxidation of the copper phases, as previously published (*11, 12*), and the ternary element (M = Pb, Sn) in the form of fine powders. (The $Cu_2Mo_6X_8$ was synthesized at high temperature using H_2-reduced molybdenum.) Samples with ratios of the ternary element to Mo_6X_8 ranging from 0.8 to 1.2 were reacted at 470 and 520°C for the sulfides and selenides, respectively. We refer to this ratio of reactants as the nominal stoichiometry. Reaction times of 1 week when M = Sn and 3 weeks when M = Pb were necessary in order to obtain single-phase samples.

We obtained lithiated compounds, with x ranging from 0.8 to 4 by reacting appropriate amounts of Mo_6X_8 and *n*-BuLi (1.6 *M* in hexane) under a helium atmosphere. After stirring for 1 day the samples were filtered and washed with ether; the filtrates were injected with a 1, 10-phenanthroline indicator to ensure that all the *n*-BuLi was consumed during the reaction. Homogeneous compounds of the resulting lithiated phases were obtained by sealing pressed powder pellets in degassed silica tubes and annealing at 450°C for 5 days. The amount of Li intercalated was obtained by atomic absorption analysis. Since these later compounds are moisture sensitive, they were always handled under a helium atmosphere. X-Ray diffraction patterns at room temperature with Cu$K\alpha_1$ radiation were obtained with the use of a holder which can be evacuated. A single phase was observed for $x \leq 1$ and $x \geq 3.0$. For intermediate values of x, two-phase mixtures were observed. A Teflon holder with a tight-fitting top was used for superconducting critical temperature (T_c) measurements by the usual low-frequency ac-susceptibility method (*17*). The T_c values of the very fine powder samples were defined as the onset of the superconducting critical temperature. The transition widths were typically 2 K, as determined by the difference between the onset temperature and the point at which the transition was 90% complete. Samples for magnetic susceptibility (200 mg) were loaded in thin-walled quartz tubing inside the glove box, evacuated, back-filled with 20 Torr of helium, and sealed prior to measurement by the Faraday technique (*18*). Four-point conductivity measurements between liquid-nitrogen and room temperature were made using powdered samples pressed into a Plexiglas die with brass plungers which served as the current leads. Finally, thermal measurements above 90 K were performed with a Perkin–Elmer differential scanning calorimeter using sealed aluminum capsules to contain the sample.

Results and Discussion

(*a*) *$Pb_xMo_6X_8$ and $Sn_xMo_6X_8$ series.* For all compounds M_xMo$_6X_8$ (M = Pb, Sn; X = S, Se) X-ray studies revealed the presence of a major phase "MMo$_6X_8$" with, depending on x, traces of secondary phases. The strong and sharp X-ray powder diffraction peaks were completely indexed on the basis of a hexagonal cell (or equivalently a rhombohedral cell). The lattice parameters obtained by least-square fitting are summarized in Tables I and II. Although the X-ray results suggest a moderate homogeneity range with sulfides or selenides DSC mea-

TABLE I

CRYSTAL DATA AND SUPERCONDUCTING TRANSITION TEMPERATURES T_c FOR THE SERIES M_xMo$_6$S$_8$ (M = Sn, Pb)

Compounds nominal composition	a_r (Å)	α_r (°)	a_h (Å)	C_h (Å)	V_h (Å)^3	T_c (K)	Observed impurity phase (X rays)	Observed impurity (DSC)
$Sn_{1.4}Mo_6S_8$	6.512	89.273	9.150(2)	11.421(1)	828.25	14	Sn	Sn
$Sn_{1.2}Mo_6S_8$	6.514	89.266	9.152(1)	11.426(2)	829.01	14.1	Single phase	Sn
$Sn_{1.1}Mo_6S_8$	6.512	89.276	9.150(3)	11.420(3)	828.25	14	Single phase	Sn
$Sn_1Mo_6S_8$	6.513	89.273	9.152(2)	11.421(1)	828.63	13.7	None	
$Sn_{0.9}Mo_6S_8$	6.512	89.273	9.150(2)	11.421(2)	828.25	14	None	None
$Sn_{0.8}Mo_6S_8$	6.513	89.270	9.147(1)	11.413(2)	828.63	14	Mo_6S_8	None
$Pb_{1.2}Mo_6S_8$	6.542	89.147	9.182(3)	11.497(1)	839.67	14	Pb	Pb
$Pb_{1.1}Mo_6S_8$	6.542	89.147	9.182(1)	11.498(3)	839.67	14.1	Pb	Pb
$Pb_{1.05}Mo_6S_8$	6.542	89.122	9.180(2)	11.503(2)	839.66	14.4	Pb	None
$Pb_1Mo_6S_8$	6.542	89.155	9.183(2)	11.497(1)	839.68	14.3	Single phase	None
$Pb_{0.95}Mo_6S_8$	6.541	89.139	9.180(1)	11.498(2)	839.28	14.1	Single phase	None
$Pb_{0.9}Mo_6S_8$	6.543	89.123	9.182(2)	11.505(2)	840.04	14.1	Mo_6S_8	None
$Pb_{0.8}Mo_6S_8$	6.546	89.180	9.190(5)	11.499(6)	841.23	14	Mo_6S_8 + broad lines	None

TABLE II

CRYSTAL DATA AND SUPERCONDUCTING TRANSITION TEMPERATURES T_c FOR THE SERIES $M_xMo_6Se_8$ (M = Sn, Pb)

Compound nominal composition	a_r (Å)	α_r (°)	a_h (Å)	c_h (Å)	V_h (Å)^3	T_c (K)	Impurity phase (X rays)	Impurity phase (DSC)	T_c of impurity phases
$Sn_{0.8}Mo_6Se_8$	6.763	89.147	9.492(2)	11.887(3)	927.68	4.2	Mo_6Se_8	None	6.5
$Sn_{0.9}Mo_6Se_8$	6.764	89.146	9.494(1)	11.888(2)	928.09	4.12	Trace of Mo_6Se_8	None	—
$Sn_{0.95}Mo_6Se_8$	6.766	89.114	9.494(1)	11.898(1)	928.89	2.90	Single phase	None	—
$Sn_1Mo_6Se_8$	6.766	89.116	9.494(2)	11.892(1)	928.89	2.80	Single phase	None	—
$Sn_{1.05}Mo_6Se_8$	6.766	89.116	9.494(1)	11.898(1)	928.89	2.80	Single phase	Sn	—
$Sn_{1.1}Mo_6Se_8$	6.766	89.114	9.494(3)	11.898(2)	928.89	2.82	Single phase	Sn	3.75
$Sn_{1.2}Mo_6Se_8$	6.766	89.122	9.494(1)	11.897(1)	928.89	2.85	Single phase	Sn	3.69
$Pb_{0.8}Mo_6Se_8$	6.792	89.063	9.526(1)	11.954(1)	939.60	3.9	Mo_6Se_8	None	6.1
$Pb_{0.9}Mo_6Se_8$	6.792	89.055	9.525(2)	11.956(1)	939.59	4.12	Mo_6Se_8	None	6.6
$Pb_{0.95}Mo_6Se_8$	6.794	88.593	9.489(1)	12.053(3)	939.96	3.38	Single phase	None	No
$Pb_1Mo_6Se_8$	6.794	88.592	9.490(3)	12.054(2)	939.96	3.25	Single phase	None	No
$Pb_{1.05}Mo_6Se_8$	6.793	88.590	9.488(2)	12.051(1)	939.55	3.2	Pb	Pb	No
$Pb_{1.1}Mo_6Se_8$	6.794	88.593	5.489(1)	12.053(2)	939.96	3.25	Pb	Pb	7.2
$Pb_{1.2}Mo_6Se_8$	6.794	88.588	9.489(2)	12.054(1)	939.96	3.25	Pb	Pb	7.2

surements show small amounts of Pb or Sn which are too small to be detected by X rays. For most samples with $x > 1$, we see the onset of an endothermic peak around 234°C (Fig. 1a) and 325°C (Fig. 1b) corresponding to the melting point of Sn and Pb, respectively. This method of second-phase determination does not work for samples prepared at higher temperatures because chalcogenide compounds rather than pure ternary metal are the impurity phases. In agreement with our previous findings (*11*, *12*), we find that the value of x cannot exceed 1 for the ternary molybdenum chalcogenide phases in which the ternary element is a large atom such as Pb, Sn, Hg, or In. These data suggest that the many compounds of nominal composition "$M_{1.2}Mo_6X_8$" reported in the literature and prepared near 1200°C are multiphase products with a predominance of MMo_6X_8 and some other phases such as MoS_2, Mo_2S_3, or M-sulfides which in small amounts cannot be detected by X-ray diffraction but which are quite apparent in the magnetic properties of some rare earth compounds such as $EuMo_6S_8$ (*19*, *20*). This removes the "puzzle" of the location of the extra 0.2 M atoms in the unit cell, since only 1.0 M

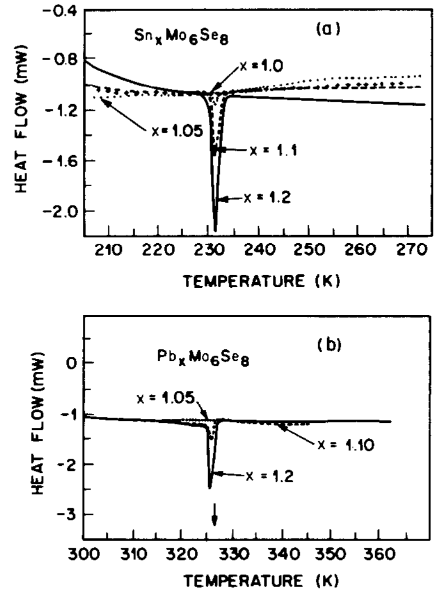

FIG. 1. Differential scanning calorimetry measurements as a function of x for the series $M_xMo_6Se_8$ (a) M = Sn; (b) M = Pb.

atoms can occupy the special positions on the $\bar{3}$ axis.

When there is a deficiency in ternary element ($x < 0.9$), X-ray diffraction patterns exhibit a low-angle peak corresponding to the 100 diffraction line of unreacted Mo_6X_8. This clearly indicates that for large size ions $M_xMo_6X_8$ has a narrow homogeneity range. These conclusions are similar to those obtained both by Marezio (*22*) and Guillevic (*23*) from single-crystal studies on $PbMo_6S_8$ or by Umarji (*21*) for $Pb_xMo_6S_8$. However, none of our compounds show a splitting of the low-angle (101) X-ray diffraction line as previously reported by Umarji *et al.* (*21*). Their extra line at 14° < 2θ < 15° probably results from the presence of MoS_2 as an impurity phase. Finally, note that the superconducting critical temperature (as well as the transition widths) also remains constant with x at 14.1 and 14 K for the lead and tin sulfide Chevrel phases, respectively.

The lattice parameters of the selenides show some change with x (Table II). An increase in α_r, more pronounced for the lead than the tin, as well as a decrease in the unit cell volume is observed as x increases from 0.9 to 0.95. Usually an increase in α_r or a decrease in unit cell volume is correlated to a decrease in T_c (*3*). The present results exhibit the opposite change in T_c (Table II). The present data show a similar trend to those obtained for $Hg_xMo_6S_8$ (*11*), where an increase in T_c with a decrease in volume has also been observed.

The homogeneity range is narrower for the sulfide than for the selenide Chevrel phases. Within the narrow homogeneity range the nonstoichiometry in the ternary element has only a small effect on the T_c. This suggests that the scatter of T_c reported in the literature for both $PbMo_6S_8$ and Sn Mo_6S_8 has another origin. Hauck (*6*) and Delk and Sienko (*10*) suggest that the nonstoichiometry in the anion X has a greater influence on the superconducting properties of these phases than the nonstoichiometry in the cation M. Another possibility is the presence of extrinsic impurities such as oxygen, since recent studies by Hinks *et al.* (*24*) have shown that oxygen substitutes for sulfur in these phases. They show that T_c is decreased by 2 K when 5 at.% of the S on the $\bar{3}$ axis is replaced by oxygen (or about 1 at.% total oxygen impurity which preferentially occupies the $\bar{3}$ site).

The breadth of the superconducting transition observed in our compounds (2 K) suggests that an oxygen impurity might be present, but that this impurity is not uniformly distributed throughout the sample. This would be expected if the impurity came from reaction of the part of the material that was in close contact with the quartz tube wall. However, the presence of this impurity does not change the conclusion that the stoichiometry range for the ternary element is quite narrow and has a maximum of $x = 1$.

(*b*) *$Li_xMo_6X_8$ series* ($X = S, Se$). The behavior of Mo_6X_8 as active cathode materials for use in nonaqueous secondary lithium cells has been investigated. At a rate of 1.0 mA/cm^2 approximately 3.4 lithium atoms per formula unit are used on discharge to approximately 1 V (Figs. 2a, b, c). These cells are readily reversible and they retain their capacity over many cycles. A loss of approximately 10% in capacity is observed after the first cycle, then the cells could be recharged to 100% of the reduced capacity for several cycles (10 is the maximum we have tried with pure Mo_6S_8 and Mo_6Se_8). With an average potential of 2 V the theoretical capacity of active material is only half that of TiS_2 (240 W h/kg for Mo_6S_8).

The electrochemical results are similar to those of Shöllhorn (*13*) and exhibit the presence of two plateaus which connect two single-phase regions near the nominal composition $x = 0.8$ and for $x > 2.7$, where the voltage composition curves have a non-

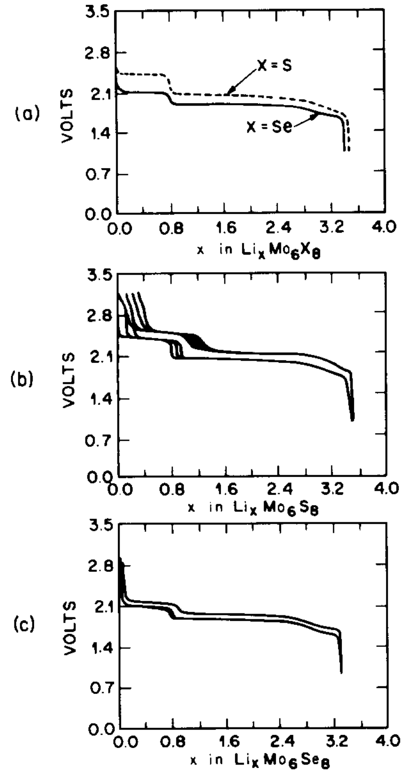

FIG. 2. Voltage vs composition for Li/LiClO$_4$, PC/Mo$_6X_8$ cells containing 30 mg of Mo$_6X_8$ (X = S, Se) discharged and charged at 100 μA. (a) First discharge, (b) and (c) represent the eighth, ninth, and tenth cycles when X = S and Se, respectively.

zero slope. The potential at the plateaus is lower for the selenides than for sulfides. This lower free energy of reaction of the selenide compared to the sulfide may be a general characteristic of these chalcogenide compounds. We were able to synthesize Hg Mo$_6$S$_8$ but not HgMo$_6$Se$_8$ (*11*). HgMo$_6$S$_8$ dissociates into Hg and Mo$_6$S$_8$ at only 500°C, so it is not surprising that a small change in the free energy of reaction between the sulfide and selenide could be enough to make formation of HgMo$_6$Se$_8$ unfavorable.

Several lithiated compositions Li$_x$Mo$_6X_8$ (X = S, Se) were prepared with x ranging from 1.0 to 4 by the n-BuLi technique (*16*). Table III contains the results of their atomic absorption analysis (Li content) and X-ray measurements of some of these. Insertion of lithium appears to occur in similar ways for Mo$_6$S$_8$ and Mo$_6$Se$_8$. Since X-ray diffraction indicates that samples at x = 1 are single phase, it is clear by comparison to the electrochemical data of Fig. 2 that approximately 20% of the cathode material does not take part in the electrochemical reaction. In order to take part in electrochemical processes each particle of the cathode material must be in electrical con-

TABLE III

CRYSTALLOGRAPHIC PARAMETERS AND SUPERCONDUCTING TRANSITION TEMPERATURES T_c AS A FUNCTION OF COMPOSITION IN THE SERIES Li$_x$Mo$_6X_8$ (X = S, Se)

Compound	Determined by atomic absorption analysis	a_r (Å)	α_r (°)	a_h (Å)	C_h (Å)	V_h (Å)^3	T_c (K)
Mo$_6$S$_8$	0	6.429	91.155	9.183	10.909	796.79	1.85
Li$_1$Mo$_6$S$_8$	1.04	6.461	92.175	9.308	10.757	807.34	5.5
Li$_3$Mo$_6$S$_8$	3.04	6.638	94.278	9.731	10.605	809.75	<1
Li$_{3.2}$Mo$_6$S$_8$[a]	3.32	6.654	94.253	9.752	10.636	876.52	<1
Mo$_6$Se$_8$	0	6.66	91.45	9.537	11.239	885.36	6.5
Li$_1$Mo$_6$Se$_8$	0.95	6.725	92.19	9.69	11.194	910.38	3.9
Li$_3$Mo$_6$Se$_8$	2.99	6.916	94.40	10.148	11.021	983.15	<1
Li$_{3.2}$Mo$_6$Se$_8$[a]	3.18	6.930	94.41	10.169	11.044	989.13	<1

[a] Samples used for neutron experiment.

tact with current collector. Apparently some of the cathode particles are electrically isolated and the experimental capacity for lithium insertion is less than that expected from the total mass of the electrode and the known maximum possible lithium content. In order to compensate for the electrically isolated cathode material, the composition scale in Fig. 2 determined by integrating the cell current, should be "shrunk" by about 20% to give the true composition. That is, the first sharp drop in potential with increasing x occurs close to $x = 1.0$. For $1 < x < 2.6$ X-ray studies indicate the presence of a two-phase region. Attempts to insert more than 3.6 Li per Mo_6X_8 unit lead to an X-ray diffraction pattern with broad lines quite different from the pattern at $x \sim 3.2$. One possible reason for a poor quality X-ray diffraction pattern is that irreversible overreduction can occur if excess *n*-BuLi is used, producing an amorphous product. However, $Li_4Mo_6S_8$ exhibits an X-ray pattern similar to $Li_{3.2}Mo_6S_8$ after being exposed a short time to air suggesting that a large, *but reversible,* structure change occurs at high lithium content. Consequently, it appears that the maximum lithium content is near $x = 4.0$, in agreement with the cell data of Fig. 3 when corrected for the electrically isolated fraction of the cathode. There is a large change in the lattice parameters (Table III) as x goes from $x = 0$ (no Li) to $x = 3$. At higher Li content α_r levels off whereas a_r increases as x increases from 3 to 3.2 for X = S, and Se, respectively. A last point to note is that insertion of only 1 Li changes both a_r and α_r significantly. The present data agree very well with those of Schöllhorn *et al.* (*13*) on similar compounds prepared using lithium in liquid ammonium instead of *n*-BuLi. We disagree with Cheung and Steele (*14*) for $Li_xMo_6S_8$ who claim that insertion of lithium in Mo_6S_8 using *n*-BuLi does not lead to a change in lattice parameters. These lithiated phases are extremely *moisture sensitive* and we have observed that a compound such as $Li_{3.2}Mo_6S_8$ after being exposed 2 hr to air has the same lattice parameters as Mo_6S_8. The mobility of lithium is rather high inside the Mo_6S_8 matrix at 300 K (*25*) and, as a result, the lithium comes out of the channels by reacting with water vapor in the air to form LiOH. This will not affect the atomic absorption analysis of lithium in these materials because the absorption measures all lithium in the sample, including any in the form of LiOH. Neutron diffraction studies of $Li_{3.2}Mo_6S_8$ by Cava *et al.* (*26*), indicate that Li randomly occupy sites similar to those occupied by copper in the channels of the Mo_6S_8.

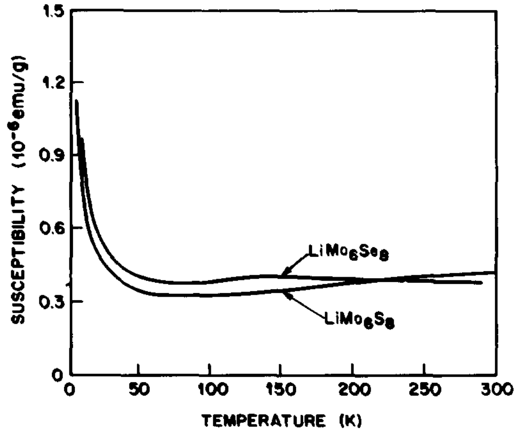

FIG. 3. The susceptibility vs temperature is shown for both $Li_1Mo_6S_8$ and $Li_1Mo_6Se_8$, respectively.

The physical properties of the single-phase compositions have also been studied. $Li_1Mo_6S_8$ and $Li_1Mo_6Se_8$ superconduct at 5 and 3.9 K, respectively, where as the lithium-rich phases ($x = 3.2$) do not superconduct. These results are not surprising, since at high Li concentrations the number of "free" electrons per Mo_6X_8 unit becomes closer to the critical value of 24, where the phase is expected to be semiconducting (*3*). Magnetic measurements reported in Fig. 3 for $Li_1Mo_6X_8$ (X = S, Se) and in Fig. 4 for $Li_{3.2}Mo_6X_8$ (X = S, Se) show a Curie-like behavior at low temperature. At $x = 3.2$ a

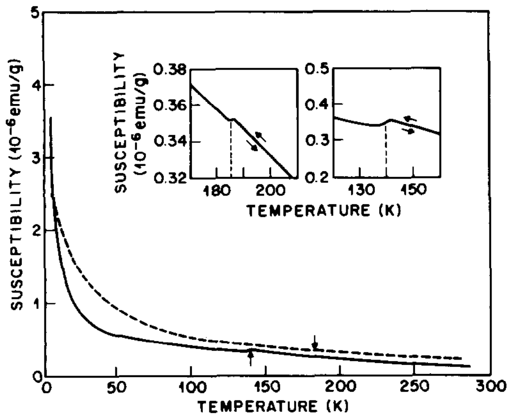

FIG. 4. Temperature-dependent susceptibility of $Li_{3.2}Mo_6X_8$ (X = S, Se). The vertical arrows exhibit the onset of a phase transition while the horizontal ones distinguish between cooling or warming of the sample.

larger Curie tail than that obtained at $x = 1$ is apparent. In addition, the magnetic susceptibility at $x = 3.2$ (Fig. 4) exhibits a small anomaly, without hysteresis, at 140 and 185 K for the sulfide and selenide, respectively. Furthermore, at the same temperature, resistivity measurements on pressed powder show a break (Fig. 5). It is likely that these anomalies are due to structural phase transitions involving an ordering of the Li. Such an ordering would lower the crystal symmetry and distort the chalcogen network and Mo_6 octahedron. A distortion of the Mo_6 octahedron could lead to a localization of the conduction electrons, which could explain the larger Curie tail observed at low temperature for $Li_xMo_6X_8$ ($x \sim 3.2$) as well as the negative temperature slope $\partial R/\partial T$ below 140 K for $Li_{3.2}Mo_6S_8$ (Fig. 5). In contrast, the positive slope found below 185 K for $Li_{3.2}Mo_6Se_8$ seems to suggest that the phase distortion affects the band structureless, in agreement with the magnetic data, since the amplitude of the variation in the density of states through the transition is at least two times smaller than the one observed for $Li_{3.2}Mo_6S_8$ (Fig. 4). A low-temperature neutron diffraction study is underway in order to better understand this phase (*27*).

Finally, we examined the reaction of ternary Chevrel phases MMo_6X_8 with Li in electrochemical cells and using *n*-BuLi. Those materials that reacted with Li did so by a displacement reaction:

$$MMo_6X_8 + 3.4n - \text{BuLi} \rightarrow Li_{3.4}Mo_6X_8 + M + \text{octane}$$

(for M = Ag, In, or Tl). After reaction the free metal M was observed by X-ray diffraction or by its melting in a DSC. Further, after one or two cycles in an electrochemical cell, the charge–discharge behavior was identical to that of $Li_xMo_6X_8$. In some cases the Li did not react (e.g., M = La or Eu). This is likely due to the lower reduction potentials of La or Eu as compared to In or Ag. These displacement reactions are simi-

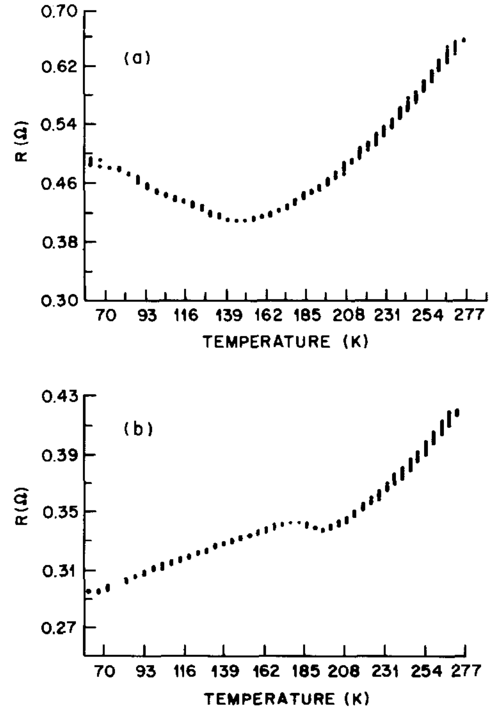

FIG. 5. Resistivity vs temperature for (a) $Li_{3.2}Mo_6S_8$ and (b) $Li_{3.2}Mo_6Se_8$. The resistivity dispersion at a given temperature comes from an artifact of the apparatus used.

lar to those reported for the reaction of $Zn_2Mo_6S_8$ with *n*-BuLi, in which a lithium Chevrel phase and dibutyl zinc are formed (*27*).

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