Lattice-parameter changes and triclinic distortions in Li$_x$Mo$_6$Se$_8$ for 0 < x < 4

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Using in situ x-ray diffraction we have measured the room-temperature structure of Li$_x$Mo$_6$Se$_8$ for 0 < x < 4. We find four single-phase regions: two rhombohedral phases and two triclinic phases. All of the structural changes are reversible with x. Features in the voltage of Li/Li$_x$Mo$_6$Se$_8$ electrochemical cells are associated with each of the structural changes.

INTRODUCTION

The Chevrel phases are ternary molybdenum chalcogenides (A$_2$Mo$_6$X$_8$; A=metal, X=chalcogen) with structures and properties that depend on A and X. Most have rhombohedral structures at room temperature and many distort to triclinic structures at low temperature. These distortions influence other properties, notably superconductivity, and have therefore received much study.

Early work on Li$_2$Mo$_6$Se$_8$ (Ref. 5) showed that x can vary between 0 and 4. Later studies showed that Li$_2$Mo$_6$Se$_8$ has a rhombohedral structure for x=0, 1, 3, and 3.2 at room temperature, with an unidentified structural distortion for x > 3.6. Recently, we showed that Li$_2$Mo$_6$Se$_8$ is single phase at room temperature for 0 < x < 1 and reported the variation with x (0 < x < 1) of the rhombohedral lattice parameters.

Here we report the room-temperature structure of Li$_x$Mo$_6$Se$_8$ for 0 < x < 4. We give details of our earlier experiments for 0 < x < 1 (Ref. 7) and present new results for 1 < x < 4. Li$_2$Mo$_6$Se$_8$ was prepared by intercalating Li into Mo$_6$Se$_8$ in electrochemical cells with beryllium x-ray windows. Thus, x could be changed in situ by charging or discharging the cell in an x-ray diffractometer. There are four distinct single-phase regions for 0 < x < 4: two rhombohedral and two triclinic phases. We have measured the variation of the lattice parameters in each of these phases. Our technique allows us to study the reversibility of the structure to changes in x, and we find that each of the rhombohedral-triclinic distortions is reversible. We also show the correlation between the structural phase transitions and features in the voltage, V(x), and -dx/dV of Li/Li$_x$Mo$_6$Se$_8$ electrochemical cells.

EXPERIMENTAL

Mo$_6$Se$_8$ was prepared from Mo foil (99.999% purity) and Se pellets (99.999% purity). Quartz ampoules containing the elements and 250 Torr of argon were sealed, then held at 1250°C for 60 h. The rhombohedral lattice parameters of our Mo$_6$Se$_8$, a=6.658 Å and α=91.76°, are in good agreement with other results.

We measured V(x) in Li/Li$_x$Mo$_6$Se$_8$ cells as described earlier. The cells were charged or discharged with a constant current while V was monitored as a function of time. In this method, changes in x are proportional to changes in time and -dx/dV is calculated by numerically differentiating V(x).

In situ x-ray diffraction experiments were made as in (Ref. 8) except that a Stoe Bragg-Brentano diffractometer controlled by a computer was used instead of a Philips instrument. The homogeneously intercalated samples are prepared by fixing V and waiting for equilibrium. Then x-ray diffraction data are collected before the voltage is stepped to a new value. x is determined either by monitoring the charge transferred to the intercalation electrode during the equilibration or from V(x).

It is difficult to align the cathodes of in situ x-ray cells exactly on the axis of the goniometer. This off-axis displacement shifts Bragg peaks from their ideal angles. The data shown in Figs. 6, 7, and 9 are not corrected for this displacement (the correction is about 0.05° at 2θ=60°) but the Bragg angles used in least-squares refinements for the lattice parameters are corrected, as are the angles in Table I.

RESULTS

Structure of Li$_x$Mo$_6$Se$_8$ for 0 < x < 1

Figure 1 shows V(x) measured for the first discharge and charge of a Li/Li$_x$Mo$_6$Se$_8$ cell at 28°C. x was determined directly from the mass of the intercalation cathode and the charge transfer. The behavior in Fig. 1 is typical of Li/Li$_x$Mo$_6$Se$_8$ cells and agrees well with data measured by Tarascon et al. The currents used correspond to a change Δx = 1 in 25 h. The results for the charge do not return x = 0 in Fig. 1 probably because some Li$_x$Mo$_6$Se$_8$ has become electrically disconnected from the cathode and because of a small side reaction for voltages near 1.7 V (see below).

A prominent feature in Fig. 1 is the abrupt drop in voltage near x = 1. Such a drop is expected when Li completely fills one type of site and begins to occupy another. For x < 1, x is less than 92°. Yvon has found that in this range of x, A atoms in A$_2$Mo$_6$X$_8$ generally occupy sites on the X axis. There is one such site per Mo$_6$X$_8$ unit and this site is full at x = 1. All such sites are full and the voltage drops.

For 0 < x < 1, V(x) for Li/Li$_x$Mo$_6$Se$_8$ cells is well described by a mean-field theory which assumes that Li
occupies only one type of site in Mo₆Se₈. Figure 2 shows an example of $V(x)$ and $-dx/dV$ at 38°C. The charge and discharge have over 200 data points, which we have joined by straight lines. The measured change in $x$ from 2.30 to 2.00 V was $\Delta x = 0.90$ for this cell. To correct for LiₓMo₆Se₈ which is electrically disconnected from the cathode, we normalize the values of $x$ to $x = 0$ and 1 at 2.3 and 2.0 V, respectively. The currents correspond to a change $\Delta x = 1$ in 50 h. The good agreement between charge and discharge shows the cell is near equilibrium and demonstrates the reversibility of intercalation for $0 < x < 1$. The solid curve in Fig. 2(b) is the mean-field prediction.\(^7\)

The mean-field theory in (Ref. 7) predicts that LiₓMo₆Se₈ is a single phase at room temperature. We have confirmed this as follows. Figure 3 shows portions of x-ray diffraction profiles taken at 22°C on the same cell at several values at $x$. The Bragg peaks shift in angle as $x$ changes but do not change in width. At each $x$ the diffraction profiles show a single phase. Figure 4 shows the variation of the rhombohedral lattice parameters for $0 < x < 1$ determined from least-squares refinements to the positions of at least 20 Bragg peaks. The changes in structure were found to be fully reversible. The linear lattice expansion in this compound leads to the long-ranged attractive interaction between lithium atoms discussed previously.\(^7\)

![FIG. 1. $V(x)$ for a Li/LiₓMo₆Se₈ cell at 28°C.](image_url)
FIG. 2. (a) $V(x)$ for a Li/Li$_{x}$Mo$_6$Se$_8$ cell at 38°C; the solid line denotes discharge, and the dashed line denotes charge. (b) $-\Delta x/\Delta V$ versus $x$ from (a). The filled square denotes discharge, and the filled circle denotes charge. The solid curve is the theoretical prediction of Ref. 7.

FIG. 3. X-ray diffraction profiles of Li$_{x}$Mo$_6$Se$_8$ taken at $x=0$, 0.32, 0.70, and 0.98. The peaks are labeled by their rhombohedral Miller indices.

FIG. 4. Variation of the lattice parameters $a$ (squares) and $c$ (circles) of Li$_{x}$Mo$_6$Se$_8$ as determined by in situ x-ray diffraction. Open symbols were measured on discharge; symbols with crosses on charge.

Structure of Li$_{x}$Mo$_6$Se$_8$ for $1 < x < 4$

For $0 < x < 1$, Li$_{x}$Mo$_6$Se$_8$ is a single phase, which we call $R_1$, with a rhombohedral structure. In contrast, there are three different phases for $x > 1$, one rhombohedral structure ($R_2$) and two triclinic structures ($T_1$ and $T_2$).

Transitions between these phases appear as peaks in $-\Delta x/\Delta V$. Figure 5 shows $-\Delta x/\Delta V$ for a Li/Li$_{x}$Mo$_6$Se$_8$ cell at 28°C. The peaks near $1.90$, $1.88$, and $1.69$ V correspond, respectively, to the transitions $R_1 < T_1$, $T_1 < R_2$, and $R_2 < T_2$. In contrast, the peak at $2.1$ V is not a phase transition; it is the behavior of the single phase $R_1$.

The large peak in Fig. 5 near $1.90$ V corresponds to a first-order phase transition between the rhombohedral phase $R_1$ with $x=1$ and the triclinic phase $T_1$ with $x=2.5$. The smaller peak at $1.88$ V corresponds to a first-order transition between the $T_1$ phase and the rhombohedral phase $R_2$. During such first-order transitions an x-ray diffraction profile shows two sets of Bragg peaks, one for each of the two coexisting phases. As an example, Fig. 6 shows portions of x-ray diffraction profiles taken...
FIG. 6. Portions of x-ray diffraction profiles near the $T_1\leftrightarrow R_2$ transition. Solid line: $T_1$ phase at 1.890 V; long-dashed—short-dashed line: $R_2$ phase at 1.870 V; dashed lined: coexistence of $T_1$ and $R_2$ phases near 1.880 V. The Miller indices of the $T_1$ and $R_2$ peaks are indicated.

FIG. 7. Portions of x-ray diffraction profiles near the $R_2\leftrightarrow T_2$ transition. (a) Solid line: 1.710 V; dashed line: 1.697 V; long-dashed—short-dashed line: 1.690 V. (b) Long-dashed—short-dashed line: 1.690 V; dashed line: 1.685 V; solid line: 1.600 V. The Miller indices of the $R_2$ and $T_2$ peaks are indicated.

FIG. 8. (a) Unit cell lengths, (b) unit cell angles, (c) unit cell volume of Li$_x$Mo$_6$Se$_8$, and (d) $-\Delta x/dV$ of Li/Li$_x$Mo$_6$Se$_8$ cells plotted versus $V$. The solid lines in (a), (b), and (c) are guides to the eye. The $T_1$, $R_2$, and $T_2$ phases are indicated. In (d), the solid curve is for the discharge and the dashed curve is for the charge.
volume of Li$_x$Mo$_6$Se$_8$ and \(-dx/dV\) of Li/Li$_x$Mo$_6$Se$_8$ cells plotted versus \(V\). The structural data in Fig. 8 were obtained by fixing the cell at successively lower voltages, so the structural data should be compared to \(-dx/dV\) for the discharge. This figure shows that the distortions occur at the peaks in \(-dx/dV\). The data in Fig. 8(d) is from a charge and discharge of a Li/Li$_x$Mo$_6$Se$_8$ cell between 1.6 and 1.9 \(V\), using currents which took 50 h to change \(x\) by \(\Delta x = 1\). The \(T_1 \rightarrow R_1\) transition starts at 1.908 \(V\); cells charged to 1.900 \(V\) are in the \(T_1\) phase.

Table I shows the results of a typical refinement to obtain the lattice parameters of the \(T_2\) phase. Figure 9(a) shows a calculated powder pattern for Li$_x$Mo$_6$Se$_8$, which can be compared to the data in Fig. 9(b). The calculation assumes that the Mo and Se atoms have the same fractional atomic coordinates as in Mo$_6$Se$_8$ (Ref. 1) and analytic approximations for their atomic scattering factors were taken from the *International Tables for X-ray Crystallography*. Gaussian peaks of halfwidth \(\Delta 2\theta = 0.20'\) were used in the calculation. The shaded peaks in Fig. 9(b) are peaks from the cell components, not Li$_x$Mo$_6$Se$_8$. We have not attempted to obtain the atom positions from Rietveld profile refinements. Even so, the good agreement shown in Fig. 9 indicates that the fractional atomic coordinates in the \(T_2\) phase are close to those of Mo$_6$Se$_8$. Similar agreement was obtained in calculations for the \(R_1\), \(T_1\), and \(R_2\) phases.

Room-temperature lattice parameters of Li$_x$Mo$_6$Se$_8$ versus \(x\) (Fig. 10) were obtained from Fig. 8 and \(V(x)\) for discharging cells. Here, the errors in our determination of \(x\) are much greater than those in Fig. 4, which were about 2%. This is because our Li/Li$_x$Mo$_6$Se$_8$ cells always took longer to discharge than to charge (using the same currents) when cycled between 1.6 and 1.9 \(V\). In Fig. 8(d), for example, the integral under the discharge (which gives \(\Delta x\)) is larger than the integral under the charge; most of this difference is in the peak near 1.7 \(V\). (The same cell design and electrolyte gave 100% Coulombic efficiency in similar experiments on other Li intercalation systems.)\(^{10,15}\) This difference between charge and discharge implies that there are side reactions in the cell, principally at low voltages, which consume Li. Since we do not know how the side-reaction current depends on \(V\), we cannot calculate \(x\) exactly.

![FIG. 10. Lattice parameters of Li$_x$Mo$_6$Se$_8$ versus \(x\) for the \(T_1\), \(R_2\), and \(T_2\) phases. The solid lines through the data points are guides to the eye and the shaded region indicates the coexistence of \(R_2\) and \(T_1\) phases. The boundaries of the shaded region are approximate.](image)

We calculate \(x\) in Fig. 10 in two steps. First we fixed \(x = 0\) at 2.3 \(V\) and \(x = 1\) at 2.0 \(V\), and calculated the value at \(x\) for the beginning of the \(T_1\) phase from the average of charges and discharges for several cells. This gives \(x = 2.5 \pm 0.2\). We then fixed \(x = 2.5\) at 1.908 \(V\) for the discharge of Fig. 8(d) and \(x = 4\) at 1.5 \(V\) and calculated \(x\). (The value of \(x = 4\) for the composition of the fully intercalated compound is the maximum value of \(x\) seen in other Chevrel compounds\(^{1}\) and agrees with Fig. 1.) Using the charge from Fig. 8(d) gave slightly different values of \(x\)—we estimate the maximum systematic error in \(x\) in Fig. 10 to be \(\pm 0.3\) near \(x = 3.3\). However, our lattice-parameter data for the \(R_2\) phase is in excellent agreement with the values reported for \(x = 3\) and \(x = 3.2\) by Tarascon et al.\(^{9}\) where the Li composition was determined by chemical analysis.

**DISCUSSION**

The rhombohedral angle \(\alpha\) has been shown by Yvon\(^{1}\) to be sensitive to the amount of delocalization of the \(A\) atom in \(A_2\)Mo$_2X_8$ from the \(\bar{3}\) axis. Here, in Li$_x$Mo$_6$Se$_8$, we find \(\alpha < 92'\) for \(x < 1\) and \(\bar{\alpha} = (\alpha + \beta + \gamma)/3 \approx 95'\) for \(x > 2.5\). We suggest that the lithium is fairly well localized in the sites at the origin of the Mo$_6$Se$_8$ unit cell (on the \(\bar{3}\) axis) for \(x < 1\) and is delocalized into sites similar to those seen for Cu$_x$Mo$_6$S$_8$ when \(x > 2.5\). As \(x\) in Li$_x$Mo$_6$Se$_8$ increases past 1, \(\alpha\) must increase in order to make more sites available for Li, because there is only 1 site on the \(\bar{3}\) axis when \(x\) is small, but 12 positions (which cannot all be simultaneously filled) when \(\alpha\) is large.\(^{1}\) Presumably the large region of coexisting \(R_1\) and \(T_1\) phases reflects the fact that Chevrel compounds with intermediate \(\alpha\) are rare.

The triclinic distortions to the \(T_1\) and \(T_2\) phases from the \(R_2\) phase both produce peaks in \(-dx/dV\) [Figs. 5

![FIG. 9. (a) Calculated and (b) measured powder x-ray diffraction profiles for Li$_x$Mo$_6$Se$_8$. See text.](image)
and 8(d)]. This indicates that the lithium is involved in the distortion because the voltage of Li/Li$_2$Mo$_6$Se$_8$ cells is proportional to the chemical potential of Li in Li$_2$Mo$_6$Se$_8$. The transitions might be order-disorder transitions involving the intercalated Li. Lithium order-disorder transitions in 2H-Li$_x$TaS$_2$ have been previously observed by a study of peaks in $-dx/dV$. For example, the $T_1$ phase might be similar to the low-temperature triclinic phase of Cu$_2$Mo$_6$S$_8$ where copper atoms fill two of the six "inner sites" in an ordered way. In Cu$_2$Mo$_6$S$_8$, this breaks the threefold symmetry and causes a triclinic distortion. The transitions might be due to an electronically driven lattice instability as in EuMo$_6$S$_8$. As Li is added to Li$_x$Mo$_6$Se$_8$, more electrons are added to the conduction band (in a rigid band picture) which may induce a lattice instability at some Li concentration. Again this should be observed as a peak in $-dx/dV$.

### Summary

We have measured the room-temperature structure of Li$_x$Mo$_6$Se$_8$ for 0 < x < 4 and have correlated the structural changes with $V(x)$ and $-dx/dV$ of Li/Li$_x$Mo$_6$Se$_8$ cells. We find four single-phase regions, two rhombohedral phases, and two triclinic phases. For 0 < x < 1, Li$_x$Mo$_6$Se$_8$ is a single phase with a rhombohedral structure. For 1 < x < 2.5, coexisting rhombohedral and triclinic phases are observed. A narrow triclinic single-phase region is found for 2.5 < x < 2.6 which coexists with a second rhombohedral phase for 2.6 < x < 2.75. This rhombohedral phase exists for 2.75 < x < 3.5 and distorts to a second triclinic phase for x > 3.6. All of the structural changes are reversible with x.

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