

Phase diagram of  $\text{Li}_x\text{Mo}_6\text{Se}_8$  for  $0 < x < 1$  from *in situ* x-ray studies

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The intercalated Li in  $\text{Li}_x\text{Mo}_6\text{Se}_8$  separates into regions of high and low concentration below a critical temperature  $T_c = 267$  K. The phase diagram agrees with a mean-field solution to a lattice-gas model of intercalation in  $\text{Li}_x\text{Mo}_6\text{Se}_8$ . The implications of this agreement are considered.

The intercalation of Li in the Chevrel compound  $\text{Li}_x\text{Mo}_6\text{Se}_8$  near room temperature is accurately described by a lattice-gas model for  $0 < x < 1$ .<sup>1-3</sup> This model predicts that the Li atoms are uniformly distributed throughout the  $\text{Mo}_6\text{Se}_8$  host in the temperature range studied in Refs. 1-3, but that they should separate into regions of high and low Li concentration at lower temperatures. The onset temperature varies with  $x$  and reaches its maximum value  $T_c$  at  $x = \frac{1}{2}$ . This phase separation, which is driven by the attractive energy of interaction between any two Li atoms in the host, has been observed in metal-hydrogen systems,<sup>4,5</sup> but these lattice-gas models describe the experiments only qualitatively.

We have observed the phase separation predicted by the mean-field theory in  $\text{Li}_x\text{Mo}_6\text{Se}_8$  and find a critical temperature of  $T_c = 267$  K. We have also measured the temperature variation of the order parameter  $\eta$  (the difference in the Li concentrations of the coexisting phases), and we find it agrees with mean-field theory. We infer the phase diagram of  $\text{Li}_x\text{Mo}_6\text{Se}_8$  from our measurement of  $\eta$ .

$\text{Li}_x\text{Mo}_6\text{Se}_8$  was made by intercalating Li into  $\text{Mo}_6\text{Se}_8$  in an  $\text{Li}-\text{Li}_x\text{Mo}_6\text{Se}_8$  electrochemical cell with a beryllium x-ray window<sup>2,6</sup> mounted in a thermostat on a powder x-ray diffractometer. Through electrical connections to the cell, we can change the Li concentration in the sample *in situ* by charging or discharging the cell.<sup>6</sup> The thermostat (shown schematically in Fig. 1) uses a thermoelectric cooler<sup>7</sup> and a 10-W heater; the temperature is fixed by controlling the heater current. A vacuum space thermally isolates the cell, and x-rays pass into the thermostat through a beryllium portion of the vacuum wall. The sample can be held at temperatures between 240 and 340 K for months with a stability of  $\pm 0.5$  K.

In  $\text{Li}-\text{Li}_x\text{Mo}_6\text{Se}_8$  cells,  $x$  is 1 and 0 when the cell voltage is 1.95 and 2.3 V, respectively.<sup>1,2</sup> The cell was cycled between 2.3 and 1.95 V several times at room temperature. The time for the charges and discharges was only 90% of the time expected from the mass of  $\text{Mo}_6\text{Se}_8$ , implying that 10% of the sample was not in electrical contact and so did not intercalate. The cell was then charged to half its capacity, to leave the connected part of the sample at  $x = \frac{1}{2}$ , then left open circuited, so that the sample could come to equilibrium. The lattice parameters agreed with those of  $\text{Li}_{0.48}\text{Mo}_6\text{Se}_8$ .<sup>1,2</sup>

X-ray diffraction profiles taken after one day at 250 K were similar to the room-temperature profiles except for

small shifts, due to thermal contraction, in the Bragg-peak positions. After several days Bragg peaks with positions that depend strongly on  $x$  were split into two peaks of roughly equal intensity. The splitting was fully developed after two weeks, which is the time needed for the phase separation to reach equilibrium at 250 K. X-ray profiles were measured at 242, 255, 260, 271, and 293 K and in each case two to three weeks were allowed for equilibrium to be reached after the temperature was changed. Figure 2(a) shows the  $(41\bar{1})$  Bragg peak obtained with copper  $K\alpha$  radiation. The  $K\beta$  radiation is removed with a Ni filter, but both  $K\alpha_1$  and  $K\alpha_2$  radiation are detected, so Bragg peaks have the standard  $K\alpha$  doublet.<sup>8</sup> Figure 2(a) shows that the  $(41\bar{1})$  doublet splits into two doublets as the temperature is lowered, but the data are complicated by the overlap of the doublets. We deconvoluted a peak shape comprised of two Lorentzians, one with twice the intensity of the other,<sup>8</sup> and separated by the  $K\alpha$  splitting. The full width at half maximum of these Lorentzians was  $0.13^\circ$ , which is the instrument resolution. As Fig. 2(b) shows, this procedure removes the  $K\alpha_2$  peaks from the profile, to reveal the splitting of the single peak into two peaks as  $T$  is reduced. We filtered the results nu-

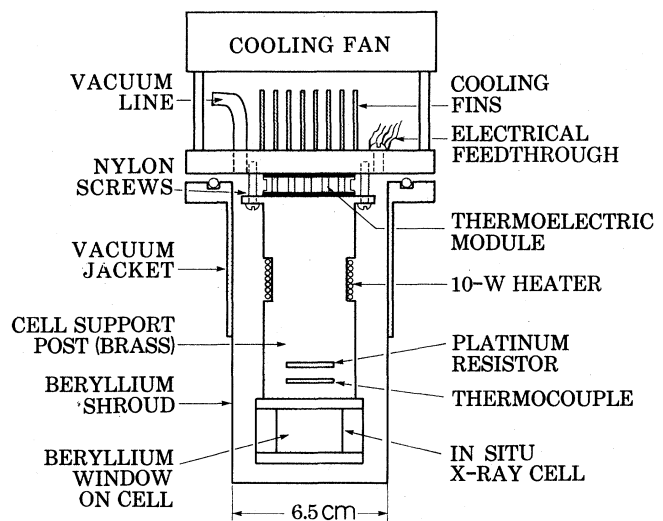


FIG. 1. A schematic diagram of the thermostat used in the experiment.

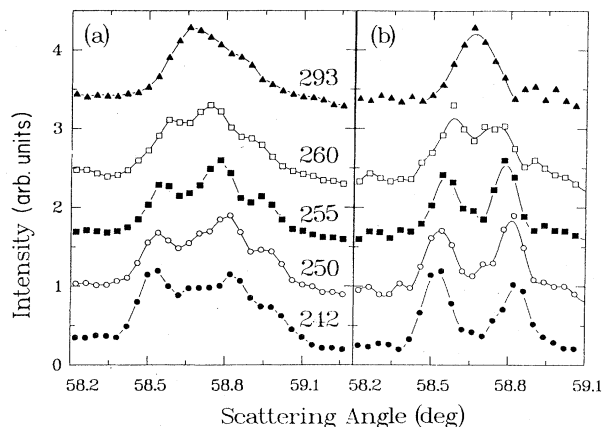


FIG. 2. (a) The  $(41\bar{1})$  Bragg peak of  $\text{Li}_{0.48}\text{Mo}_6\text{Se}_8$  at 242, 250, 255, 260, and 293 K. (b) Same as in (a) except that the  $K\alpha_2$  peaks have been removed as described in the text.

merically to reduce the noise; this filtering determines the width of the narrowest peaks in Fig. 2(b).

At the lowest temperature (242 K), eight Bragg peaks from each of the coexisting phases were resolved well enough to be used in refinements of the lattice parameters. The lattice parameters obtained were close to those for  $\text{Li}_{0.25}\text{Mo}_6\text{Se}_8$  and for  $\text{Li}_{0.75}\text{Mo}_6\text{Se}_8$  at room temperature,<sup>1,2</sup> showing that the Li had indeed separated into high- and low-density regions, but did not agree exactly with the room-temperature values, presumably because of thermal contraction.

To derive the order parameter  $\eta$  the rhombohedral lattice parameters,  $a$  and  $\alpha$ , of  $\text{Li}_x\text{Mo}_6\text{Se}_8$  for  $0 < x < 1$  (Refs. 1 and 2) were fit with the polynomials:

$$a = (6.6575 + 0.06385x) \text{ \AA}$$

and

$$\alpha = (91.766 + 0.1378x + 0.1453x^2) \text{ deg}.$$

Then the rate of change of the scattering angle  $2\theta$  of each Bragg peak with  $x$ ,  $2(\partial\theta/\partial x)_T$ , was calculated as a function of  $x$ . For the Bragg peaks  $(41\bar{1})$ ,  $(600)$  and  $(5\bar{3}2)$ ,  $2(\partial\theta/\partial x)_T$  varies monotonically by less than 4% for  $0 < x < 1$  and is  $0.61^\circ$ ,  $1.01^\circ$ , and  $1.22^\circ$  at  $x = \frac{1}{2}$ , respectively. Other Bragg peaks had either a smaller  $2(\partial\theta/\partial x)_T$ , a large variation in  $2(\partial\theta/\partial x)_T$ , or lower intensity. We measured the splitting between the Bragg peaks of the coexisting phases for the Miller indices above and used the values of  $2(\partial\theta/\partial x)_T$  at  $x = \frac{1}{2}$  to obtain  $x_2 - x_1 = \eta$  shown in Fig. 3. This assumes the thermal expansion coefficient is independent of  $x$ . The thermal expansion of  $a$  at  $x = 0.48$  is  $10.1 \times 10^{-6} \text{ K}^{-1}$  (from the 271 and 293 K data). Variations with  $x$  of up to 50% in the thermal expansion do not affect the errors bars in Fig. 3; these errors arise mainly from measuring the peak splitting.

The lattice-gas model<sup>1-3</sup> that describes the electrochemical behavior of  $\text{Li-Li}_x\text{Mo}_6\text{Se}_8$  cells also describes the data of Fig. 3. In the model, the free energy  $F$  is

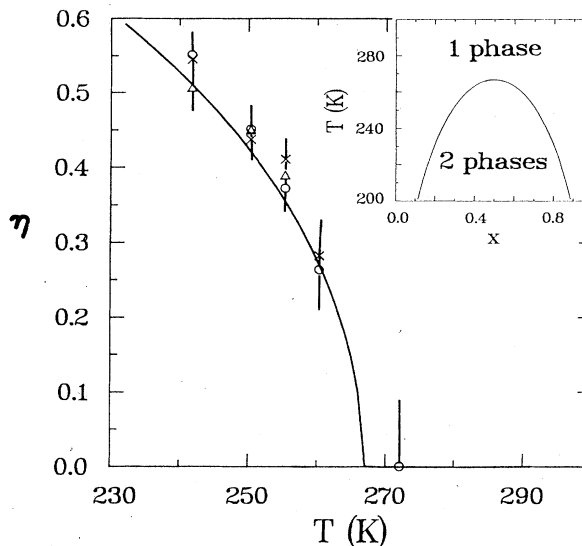


FIG. 3. The order parameter  $\eta$  versus temperature. ( $\eta$  is the difference between the Li concentrations of the coexisting phases.) The data points were determined from the  $(41\bar{1})$  (circles),  $(5\bar{3}2)$  (crosses), and  $(600)$  (triangles) peaks. The solid curve is the prediction of the model described in the text for  $T_c = 267$  K. The inset shows the theoretical phase diagram for  $T_c = 267$  K.

$$F/N = E_0x + Ux^2/2 + kT[x \ln(x) + (1-x)\ln(1-x)]. \quad (1)$$

Here  $N$  is the number of available sites in the host,  $E_0$  is the binding energy of a Li atom to one of these sites,  $U/N$  is the energy of interaction between any two Li atoms intercalated in the host, and  $k$  is Boltzmann's constant. This expression is equivalent to a mean-field solution to the lattice-gas model.<sup>1</sup> Phase separation occurs for  $T < T_c = |U|/4k$  when  $U$  is negative.<sup>9</sup> The compositions of the coexisting phases below  $T_c$ ,  $x_1$  and  $x_2$ , are given by

$$x_1 = \frac{1}{2} - \eta/2$$

and

$$x_2 = \frac{1}{2} + \eta/2,$$

where

$$\eta = \tanh[(T_c/T)\eta]. \quad (2)$$

The phase diagram in the temperature-composition plane is the variation of  $x_1$  and  $x_2$  with  $T$ , shown in the inset of Fig. 3 for  $T_c = 267$  K. The solid curve in Fig. 3 is the prediction of Eq. (2) for the same  $T_c$ . Our results measure only the difference  $x_2 - x_1$ , not the average, so we cannot prove that the experimental phase diagram is symmetric about  $x = \frac{1}{2}$ , but the lattice-parameter refinements at 242 K limit the asymmetry at that temperature to

$$(x_2 + x_1)/2 = \frac{1}{2} \pm 0.1.$$

We expect that the experimental phase diagram is symmetric because  $-(\partial x/\partial V)_T$  vs  $x$  is symmetric,<sup>1</sup> as discussed below.

The value of  $T_c = 267$  K used to fit the data of Fig. 3 is 1.5% larger than that calculated from  $U$  measured earlier by fits to electrochemical data above  $T_c$ .<sup>1</sup> Those experiments used  $\text{Mo}_6\text{Se}_8$  made in a different batch, so we repeated the electrochemical measurements on the material used here. Figure 4 shows  $-(\partial x/\partial V)_T$  vs  $x$  at 301 K and the theoretical prediction<sup>1</sup> for  $T_c = 267$  K. Note that  $-(\partial x/\partial V)_T$  is almost symmetric about  $x = \frac{1}{2}$ . For this material, the same theory describes the order parameter below  $T_c$  and the electrochemical data above  $T_c$ . We do not know why  $T_c$  and  $U$  vary between batches, but since  $U$  is believed to be related to the elastic constants of the host,<sup>1</sup> this variation could be caused by some dependence of the elastic properties on the growth conditions.

The success of mean-field theory in describing  $\text{Li}_x\text{Mo}_6\text{Se}_8$  implies that the Li-Li interaction is of long range and is probably caused by the strain fields set up by intercalated Li atoms.<sup>1</sup> Our electrochemical measurements between 278 and 318 K agree with the theoretical expressions to within experimental error, but similar experiments at lower  $T$  would take several months because the diffusion of Li in the host slows as  $T$  decreases. The errors in  $\eta$  (Fig. 3) are large and the resolution of our diffractometer makes experiments nearer to  $T_c$  impossible. Within the errors, the mean-field expressions fit the data. Although this transition appears to be mean-field-like, other experiments near  $T_c$  are needed to investigate any possible corrections to mean-field theory.

The kinetics of the phase separation are slow for several reasons. First, during phase separation Li atoms diffuse over large distances within the host crystallites. These distances must be at least several hundred angstroms, owing to the sharpness of the Bragg peaks from the coexisting phases. Second, the diffusion constant  $D$  of Li must decrease as  $T$  decreases. (To our knowledge,  $D$  has not been measured in this material, although our electrochemical measurements suggest it is about  $10^{-9}$  cm<sup>2</sup>/sec at room temperature.) Finally, near  $T_c$ , the driving force for the phase separation becomes small, leading to critical slowing down.<sup>5</sup>

Theoretical work on metal hydrides shows that phase diagrams depend on the interface between the coexisting phases.<sup>4,5</sup> When the lattices are coherent, the mismatch of the lattice parameters produces elastic stress. The associated elastic energy modifies the phase diagram from that expected for an incoherent interface, when such

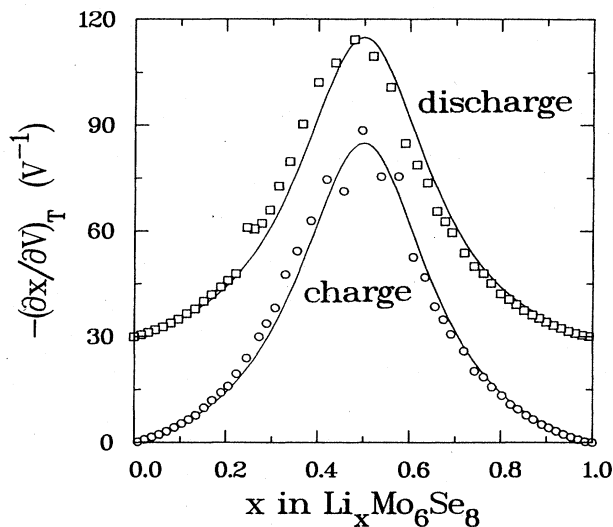


FIG. 4.  $-(\partial x/\partial V)_T$  vs  $x$  for  $\text{Li-Li}_x\text{Mo}_6\text{Se}_8$  cell at 301 K cycled at a current for which  $x$  changed by 1 in 100 hours. The circles were measured during charge and the squares during discharge. The solid curves are the predictions of the theory for  $T_c = 267$  K. The discharge has been offset by  $30 \text{ V}^{-1}$  for clarity.

stresses are relaxed by dislocations. The lattice-gas model does not consider such effects, so the agreement between theory and experiment implies that the phases in  $\text{Li}_x\text{Mo}_6\text{Se}_8$  are incoherent.

We have also found that  $\text{Li}_x\text{Mo}_6\text{S}_8$  is two coexisting phases at 250 K, but we have not determined  $T_c$ . This compound is single phase for  $0 < x < 1$  at room temperature.<sup>10</sup> We expect that the model that describes  $\text{Li}_x\text{Mo}_6\text{Se}_8$  will also describe the sulfide.

Many Chevrel phases, such as  $\text{Pb}_x\text{Mo}_6\text{S}_8$ , have been prepared only with  $x=0$  and  $x=1$  at room temperature.<sup>11</sup> We suggest that the phase diagram of such Chevrel compounds may be similar to that of  $\text{Li}_x\text{Mo}_6\text{Se}_8$  except with a much higher  $T_c$ . Then metastable Chevrel phases with intermediate values of  $x$  might be prepared by rapid quenching from high temperatures where the material for these values of  $x$  is a single phase.

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