Lithium intercalation in $Li_xMo_6Se_8$: A model mean-field lattice gas

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We show that lithium intercalation in $Li_xMo_6Se_8$ is described accurately by mean-field solutions to a *single-parameter* lattice-gas model. We present mean-field fits to the inverse derivative dx/dV of the voltage V of $Li/Li_xMo_6Se_8$ cells at several temperatures. This is apparently the first fully quantitative description of dx/dV for an intercalation system and the first realization of a three-dimensional mean-field lattice gas.

Models of the Ising type have been used to describe many physical systems—intercalation systems, adsorbed species, binary alloys, and magnetic systems are examples. For dimensions higher than one the model cannot be solved exactly except in special cases, such as when the range of interactions becomes infinite.[1] Most solutions to Ising models are therefore based on approximate methods, the simplest of which, mean-field theory (MFT), is equivalent to assuming interactions of infinite range. MFT predicts some features of Ising systems, such as spontaneous ferromagnetism below a critical temperature T_c, but calculations of thermodynamic quantities usually agree only qualitatively with experiments. Reports of excellent agreement with the predictions of MFT exist for some magnetic systems,[2] but the origins of the long-ranged magnetic interactions are unclear. We show that intercalation in $Li_xMo_6Se_8$ can be described accurately by a three-dimensional lattice-gas model with infinite-ranged attractive interactions between intercalated lithium atoms. We find excellent agreement between $-dx/dV$ (the response in lithium concentration x to changes in the voltage V of $Li/Li_xMo_6Se_8$ cells[3]) and the predictions of a *single-parameter* MFT. This is apparently the first quantitative description of the variation of $-dx/dV$ for an intercalation battery, although various qualitative or semiquantitative ones exist.[4,5] An estimate of the long-range interaction between intercalated atoms due to the elastic expansion of the lattice during intercalation is in rough agreement with measurement.

Many Chevrel phases, $A_xMo_6X_8$ (A = metal, X = S, Se, Te) have been previously studied for $0<x<4$ (Ref. 6). Mo_6Se_8 is rhombohedral, with space group $R\bar{3}$ (C_{3i}^2), and lattice parameters $a=6.658$ Å and $\alpha=91.58°$. The arrangement of the Mo_6Se_8 clusters gives rise to a three-dimensional network of "tunnels" in which the A atoms of $A_xMo_6Se_8$ reside. Large atoms, like lead in $PbMo_6Se_8$, occupy positions on the $\bar{3}$ axis between Mo_6Se_8 clusters. These positions (one per Mo_6Se_8 formula unit) form a slightly distorted simple cubic lattice with the same lattice parameters as Mo_6Se_8. Lithium atoms probably occupy these positions for $0<x<1$. For $x>1$ the lithium is expected to occupy positions similar to those found for smaller atoms like Fe, Ni, or Co (Ref. 7).

Mo_6Se_8 was prepared in pure form by the direct reaction of Mo foil (99.999% purity) and Se pellets (99.99% purity) in sealed quartz ampoules for 60 h at 1250 °C. Figure 1 shows $V(x)$ for a $Li/Li_xMo_6Se_8$ electrochemical cell constructed as described previously.[8] The results agree well with Tarascon *et al.*[9] The voltage was measured as the cell was charged and discharged at constant current. Values of x were determined from the mass of the intercalation cathode and the charge transfer, and have not been adjusted in any way. The currents corresponded to a change $\Delta x=1$ in 25 h. The results do not return to $x=0$ in Fig. 1, most likely because some $Li_xMo_6Se_8$ becomes electrically disconnected from the cathode. The length of the first plateau, $\Delta x=1$, suggests this portion of the discharge correponds to the filling of the sites on the $\bar{3}$ axis. If so, the second plateau, at lower voltage, corresponds to the filling of other sites.

Figure 2 shows the lattice parameters of $Li_xMo_6Se_8$ for $0<x<1$ determined from *in situ* x-ray diffraction studies using electrochemical cells with beryllium windows.[10] These values of x were normalized to $x=0$ and $x=1$ at 2.3 and 2.0 V, respectively. The continuous and reversible changes in a and α indicate that for $x<1$, $Li_xMo_6Se_8$ is a single phase at room temperature. For $x>1$ we find two regions of coexisting phases and a single phase region. Details of these experiments will be given elsewhere.[11]

To explain $V(x)$ for $x<1$ consider a simple cubic lattice gas. In MFT the chemical potential μ and $-dx/dV$ are[4]

$$\mu=-eV=E_0+\gamma Ux+kT\ln[x/(1-x)]$$

and

$$\frac{dx}{d\mu}=\frac{-1}{e}\frac{dx}{dV}=\left[\gamma U+\frac{kT}{x(1-x)}\right]^{-1}.$$

Here E_0 is the energy associated with the filling of an isolated lattice site, γ is the number of sites coupled to a given site by the interaction U, k is Boltzmann's constant, and T

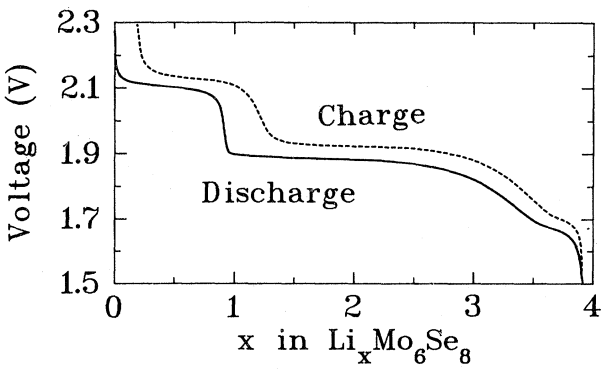

FIG. 1. $V(x)$ for a $Li/Li_xMo_6Se_8$ cell.

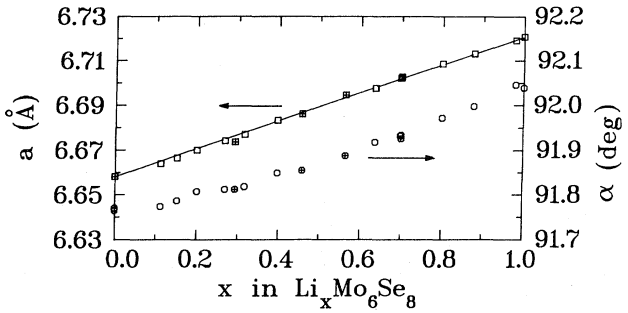

FIG. 2. Variation of the lattice parameters, a (squares) and α (circles) of $Li_xMo_6Se_8$ as determined by *in situ* x-ray diffraction. Open symbols were measured on discharge; symbols with crosses on charge.

is the temperature. MFT is exact when any pair of atoms interact with energy U, i.e., as $\gamma \to \infty$ with $\gamma U = \text{const}$. Comparisons between $-dx/dV$ vs x measured at several temperatures [by numerically differentiating $V(x)$] and the predictions of MFT with an attractive interaction, $\gamma U = -0.0904$ eV, are shown in Fig. 3. (The data were normalized to $x=0$ at 2.3 V and $x=1$ at 2.00 V.) The *single parameter* γU describes the data at all three temperatures. Figure 3 shows data measured from the charge of $Li/Li_xMo_6Se_8$ cells; data measured on discharge show equal agreement with the MFT.

Fitting $-dx/dV$ vs V or x is equivalent to fitting the magnetic susceptibility versus magnetic field or magnetization, respectively, for magnetic systems. All the spins in a ferromagnet above T_c can rarely be aligned in practical fields, equivalent to $x=0$ or $x=1$ in a lattice gas. Comparisons of theory and experiment (like Fig. 3) are usually impossible for magnetic systems where typically only the temperature dependence of the zero-field suspectibility (corresponding to $-dx/dV$ at $x=\frac{1}{2}$ in the lattice gas) is measured.

The expressions above predict $-dx/dV$ should diverge, and phase separation (analogous to spontaneous magnetization in a ferromagnet) should occur for $T < T_c = \gamma U/4k$. For $\gamma U = -0.0904$ eV, $T_c = -10\,^\circ$C. We find $-dx/dV$ is sensitive to the range of the attractive interactions even above T_c. Figure 4 compares the mean-field predictions for $-dx/dV$ with $\gamma U = -0.089$ eV with the results of Monte Carlo simulations using standard methods.[12] A $10\times10\times10$ simple cubic lattice with periodic boundary conditions was used for the Monte Carlo simulations. The nearest-neighbor interaction $U' = -0.1078/6$ eV gives the same peak height as MFT as 28 °C. The Monte Carlo results do not reproduce the shape of the data (which is accurately described by MFT) nor the variation of peak height with temperature. The success of MFT indicates that the Li atoms are randomly distributed for $T > 10\,^\circ$C and do not exhibit short-range order as they do in the Monte Carlo calculations. However, this does not imply that the Li-Li interaction is exclusively long range. We found, for example, that by splitting the total interaction into a long-range part, U'', and a nearest-neighbor part, U', such that $\gamma U = \gamma U'' + 6U'$, equally good fits to the data for any $|U'| < |\gamma U''/6|$ were obtained. For larger $|U'|$, however, the fits worsened and we conclude that a substantial fraction of the total interaction energy must be long range.

Theoretical work shows that linear lattice expansion leads to a concentration-independent attractive interaction between pairs of intercalant atoms which is independent of the distance between the atoms.[13–15] Using the results of Ref. 14 for an elastic continuum and the measured bulk modulus of Mo_6Se_8 (Ref. 16) we can make a theoretical estimate for γU. The energy of interaction for two dilation centers in a sphere of volume v, with one at the center, if the surface of

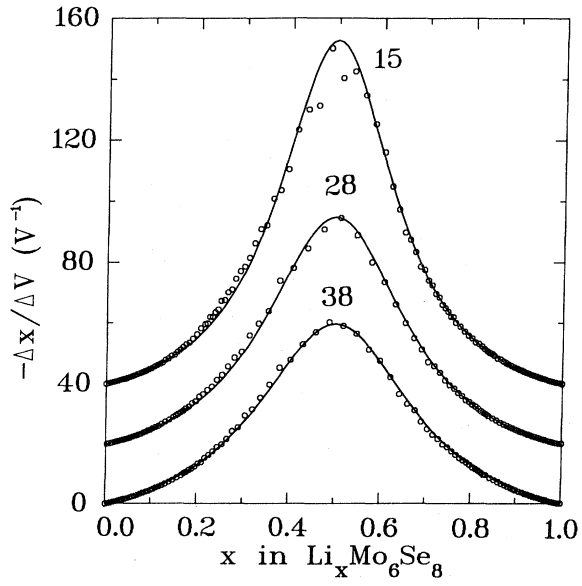

FIG. 3. $-dx/dV$ vs x measured (○) for $Li/Li_xMo_6Se_8$ cells at the Celsius temperatures indicated. The currents used corresponded to a change $\Delta x = 1$ in the following times: 15 °C, 100 h; 28 °C, 50 h; and 38 °C, 50 h. The solid lines are the predictions of the mean-field theory described in the text. The data and calculations for 28 and 15 °C have been offset by 20 and 40 V^{-1}, respectively, for clarity.

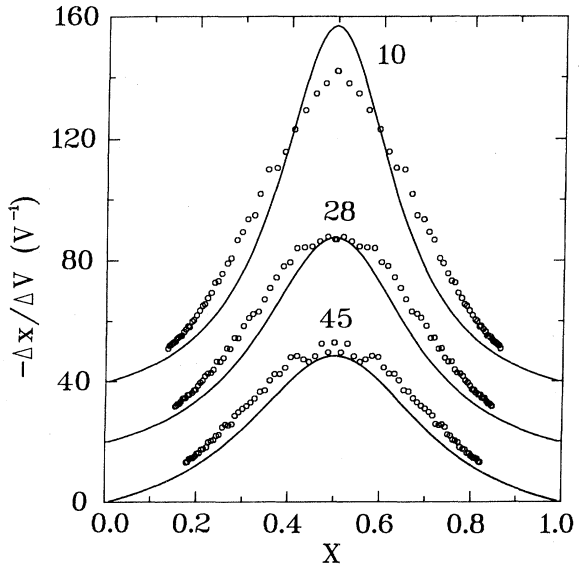

FIG. 4. $-dx/dV$ vs x predicted by mean-field theory (——) and Monte Carlo simulations with nearest-neighbor interactions (○) at different Celsius temperatures. The calculations for 28 and 10 °C have been offset by 20 and 40 V^{-1}, respectively, for clarity.

the sphere is either clamped or free, is

$$U_f = \frac{-1}{v} 9B^2 \left(\frac{\epsilon_0}{\rho_0}\right)^2 \left(\frac{1}{B} - \frac{1}{C_{11}}\right) \quad \text{(free)} ,$$

$$U_c = \frac{+1}{v} 9B^2 \left(\frac{\epsilon_0}{\rho_0}\right)^2 \frac{1}{C_{11}} \quad \text{(clamped)} .$$

Here, B is the bulk modulus, ϵ_0 is the strain per unit concentration, ρ_0 is the density of dilation centers at unit concentration, and C_{11} is a component of the stiffness tensor. Because C_{11} is unknown, we calculate the difference between U_f and U_c and find

$$N(U_f - U_c) = -9B\frac{\epsilon_0^2}{\rho_0} = -0.0509 \text{ eV}$$

for $Li_xMo_6Se_8$. This continuum estimate is in rough agreement with $\gamma U = -0.0904$ eV needed to fit the data and suggests that the infinite-range part of the interaction is of elastic origin.

In the metal hydrides, where the elastic interaction is important, short-range interactions cause significant departures from MFT.[17] In $Li_xMo_6Se_8$, where the nearest-neighbor Li-Li distance is about 6.7 Å (much larger than the H-H distance in PdH_x, 2.8 Å) for $x < 1$, the Coulomb interaction is expected to be well screened because of the high density of states at the Fermi level.[6]

This system provides a unique test for theories of lattice gases. For example, the diffusion constant of lithium in $Li_xMo_6Se_8$ could be compared with existing theories.[18] In addition, low-temperature diffraction experiments on $Li_xMo_6Se_8$ will clarify the predicted phase separation. The effects of lattice parameter mismatch below T_c may lead to a phase diagram significantly different from that predicted by MFT if the strains are coherent.[14]

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