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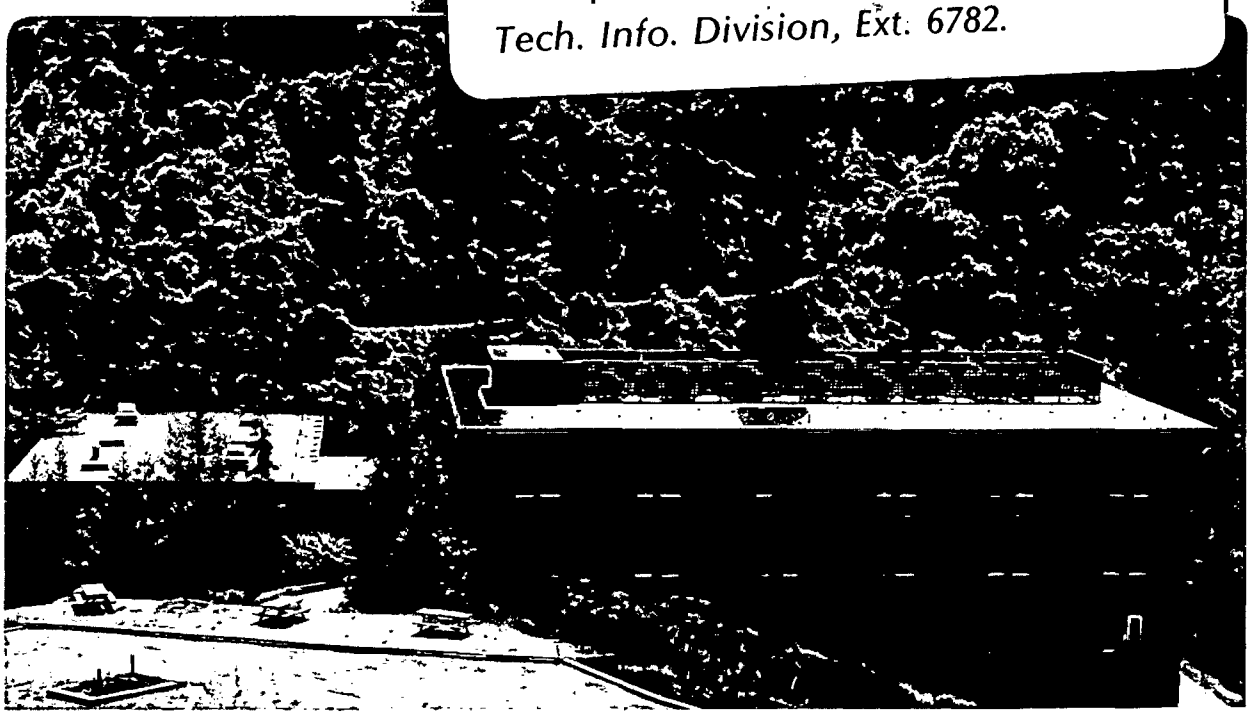

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Effect of disorder on the Li intercalation properties of $Li_xTa_yTi_{1-y}S_2$: A mean-field theory

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A mean-field approximation is applied to a triangular-lattice gas model with three different site energies randomly distributed and nearest-neighbor pairwise repulsion. The model is intended to represent intercalated Li in $Li_xTa_yTi_{1-y}S_2$. Ground-state diagrams show various sequences of ordered phases. Finite temperature results show minima in the "incremental capacity" curves due to nearly complete filling of sites of a given chemical type. The model is good for those alloys where the experimental results suggest a disordered distribution of Li atoms.

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1. INTRODUCTION

In this paper we present a generalized mean-field theory for a triangular lattice gas with sites of different chemical type randomly distributed. The particles in the lattice gas are assumed to interact throught a nearest-neighbor repulsion only. The model is applied to Li intercalated in $Ta_yTi_{1-y}S_2$, where different chemical types of sites available for Li occupation are caused by the distribution of the host Ta and Ti atoms.

Triangular lattice gas models have been applied recently[1-3] to the problem of Li^+ ordering in Li_xTiS_2. This compound can be produced by means of a highly reversible electrochemical cell, which consists of a Li anode and a TiS_2 cathode connected by an external circuit and an appropriate electrolyte. During discharge, Li ions travel through the electrolyte and are intercalated in TiS_2, while electrons (one per Li ion) travel through the external circuit and are donated to the TiS_2 conduction band. The voltage V of such a cell is given by

$$eV = (\text{constant} - \mu_1) \quad , \qquad (1)$$

where μ_1 is the Li^+ chemical potential in Li_xTiS_2 and the Li anode is considered a Li^+ reservoir.

Accurate measurements have been performed[4] of the V-vs.-x relationship in Li/TiS_2 batteries at constant tempera-

ture. Features of the dependency of incremental capacity ($-\partial x/\partial V$) on $\underline{x}$ have been explained qualitatively and semi-quantitatively by the two-dimensional lattice gas models[1,3]: some minima are associated with ordered structures at low temperature while sharp peaks (divergences) are due to order-disorder transitions.

In the $Ta_yTi_{1-y}S_2$ series ($0 \leq y \leq 1$), the atoms of Ta and Ti are supposedly randomly distributed in the material[5,6], which belongs to the same 1T polytype of TiS_2. The sites available for Li intercalation reside between two S--transition metal--S sandwiches and have an octahedral coordination of six S atoms. These sites make themselves a 2-D triangular network. For $Li/Ta_yTi_{1-y}S_2$ batteries, strikingly different incremental capacity curves[5] between the cases y = 0 and y = 1 indicate different types of interactions between Li ions when intercalated in TiS_2 and TaS_2, with a possible strong contribution of crystal distortions[7,8] for TaS_2. For $y \leq 0.5$ the main effects of the substitution of Ta for Ti atoms in the host are lower values for the voltage for all $\underline{x}$ and smoother incremental capacity curves. It is clear that different guest-host interactions play an important role in the evolution of such incremental capacity curves as $\underline{y}$ is increased.

The lithium atoms in $Li_xTa_yTi_{1-y}S_2$ interact in two different ways. The predominant interaction is the Coulomb pairwise repulsion, strongly screened by the electrons in

the host and, for a given y, probably x-dependent[3]. There are also interactions mediated by a strain field produced by dilation of the host structure during intercalation. The introduction of such elastic energy contributions[9] with the possibility of an imperfect order along the c axis involves a number of further adjustable parameters and is ignored in this paper.

2. GENERALIZED MEAN-FIELD THEORY FOR RANDOMLY DISTRIBUTED SITE ENERGIES

In the case of $Li_xTa_yTi_{1-y}S_2$, we consider only the effect of the transition-metal atoms directly above and below each site available for Li occupation. We divide the lattice into three "chemical types" with energy E_σ and number of sites (Np_σ). Here $\sigma = 0,1,2$ denotes the sites that lie between two Ti atoms $\left[p_0=(1-y)^2\right]$, between one Ta and one Ti $\left[p_1=2y(1-y)\right]$, and between two Ta $\left[p_2=y^2\right]$. We also assume that the replacement of a Ta for a Ti contributes a term E_1 to E_σ, so that

$$E_\sigma = E_0 + \sigma E_1 \quad . \tag{2}$$

The value of E_0 yields a constant voltage to the voltage-composition relations and does not affect the form of the incremental capacity curves. Therefore we take $E_0 = 0$ for simplicity.

Since the voltage drops in general when $\underline{y}$ increases, we conclude that Li is less easily intercalated when Ta atoms replace Ti atoms. This indicates a positive value for E_1 in Eq. (2). We estimate $E_1 \sim 10^{-1}$ eV from the difference between the free energies of formation[5] (i.e. the integrals of the voltage-composition relations) of Li_1TiS_2 and Li_1TaS_2. This is of the same order of magnitude of the nearest-neighbor repulsion $\underline{U}$ between the Li ions required for a reasonable fitting[3] of the incremental capacity of Li_xTiS_2. We must keep in mind that $\underline{U}$ may depend on $\underline{y}$, since different host lattices contribute differently to the screening of the Li-Li repulsion. The dependency of $\underline{U}$ on $\underline{x}$ is neglected in the present model.

The triangular lattice of nearest-neighbor separation $\underline{a}$ is divided into three interpenetrating triangular sublattices α, β and γ of nearest-neighbor separation $3^{1/2}\,\underline{a}$. Ordered structures are described by the predominant occupation of one of the sublattices. Each of the sublattices ν has a number $(Np_\sigma/3)$ of sites of chemical type σ and, by definition, $(Nd_{\nu\sigma}/3)$ such sites that are occupied. We also define the variables n_ν and c_σ according to Table 1. The total lattice has Nx occupied sites and N(1-x) empty sites. The following constraints hold for the occupation variables $d_{\nu\sigma}$:

$$0 \le d_{\nu\sigma} \le p_\sigma \;; \tag{3a}$$

$$\sum_\nu d_{\nu\sigma} = 3c_\sigma \;; \tag{3b}$$

$$\sum_\sigma d_{\nu\sigma} = n_\nu \;; \tag{3c}$$

$$\sum_{\nu\sigma} d_{\nu\sigma} = 3x \;. \tag{3d}$$

In the mean-field approximation, the expression for the entropy is

$$S = k_B \ln \prod_{\nu\sigma} \frac{(Np_\sigma/3)!}{(Nd_{\nu\sigma}/3)![N(p_\sigma - d_{\nu\sigma})/3]!} \;, \tag{4}$$

while the energy of the lattice is given by

$$E = NU\left(n_\alpha n_\beta + n_\beta n_\gamma + n_\gamma n_\alpha + \sum_\sigma \psi_\sigma c_\sigma\right) \;; \tag{5}$$

here we define

$$\psi_\sigma \equiv \frac{E_\sigma}{U} = \frac{\sigma E_1}{U} \;.$$

Given $\underline{y}$, μ, τ and ψ_1, the nine occupation probabilities $\{d_{\nu\sigma}\}$ are independent variables for the minimization of the reduced grand potential

$$\omega = \frac{E}{NU} - \tau\frac{S}{Nk_B} - x\mu \quad , \tag{6}$$

where

$$\tau = \frac{k_B T}{U} \quad , \quad \mu = \frac{\mu_1}{U} \quad . \tag{7}$$

3. GROUND-STATE DIAGRAMS

At zero temperature the present model can be solved by minimizing the quadratic form (5) for the energy with the restrictions of Eq. (3), at given $\underline{y}$, $\underline{x}$ and ψ_1. In general, the solution defines a point in $d_{\nu\sigma}$-space where all but one of the $\{d_{\nu\sigma}\}$ either are zero or assume their maximum possible value p_σ. Given $\underline{y}$ and ψ_1, the concentration ($\underline{x}$) axis is then divided into several intervals, each of them having only one $d_{\nu\sigma}$ varying (linearly) with $\underline{x}$. This picture is always valid for small or large ψ_1, compared to unity. For $\psi_1 \sim 1$, however, the curve (i.e., the continuous set of straight-line segments) $\underline{E}$ vs. $\underline{x}$ is not always concave. Lines of lower energy can then be drawn which are tangents to the original curve. This procedure defines intervals of coexistence of phases. Once this method is applied to many values of ψ_1, at given $\underline{y}$, a phase diagram can be obtained in the (x, ψ_1) plane.

Fig. 1 displays such a diagram for $y = 1/3$ and $1/2$. Shaded regions represent two-phase mixtures. For each single-phase region the indices $\nu\sigma$ give the only occupation variable ($d_{\nu\sigma}$) that varies with $\underline{x}$, while all others equal either 0 or p_σ. The diagrams are relatively simple for specific values of $\underline{y}$ (e.g., 1/2 and 1/3), but they become quite elaborate for general values of $\underline{y}$. The symmetry of the equation for the energy allows us to obtain diagrams for $y > 1/2$ from the ones for $y < 1/2$. The diagram for $(1-y)$ results from reflecting the diagram for $\underline{y}$ about $x = 1/2$; we must also change sublattices $\alpha \leftrightarrow \gamma$ and chemical types $0 \leftrightarrow 2$.

The sequence for filling the $\nu\sigma$ sites, as the lattice is filled from $x = 0$ to 1, at given ψ_1, can be obtained from ground-state diagrams like the one of Fig. 1. Especially simple sequences, with no two-phase intervals, occur in the limits $\psi_1 \ll 1$ and $\psi_1 \gg 1$. In the first case the sublattices are completely filled in succession. In the second case the division into chemical types predominates over the sublattice representation, and there are spatially disordered ground-state structures at $x = p_0$ and $x = (1-p_2)$.

In the single-phase intervals (at given $\underline{y}$ and ψ_1), the free energy $F=(E-TS)$ becomes a smooth function of $\underline{x}$ at finite τ. The zero-temperature incremental capacity is determined by the limiting behavior of the entropy. Between two critical points, x_n and x_{n+1}, that determine a ground-state single-phase interval, we have

$$\lim_{\tau \to 0} \tau \frac{\partial x}{\partial \mu} = \frac{(x-x_n)(x_{n+1}-x)}{x_{n+1}-x_n} \quad , \tag{8}$$

i.e., the reduced incremental capacity is a simple parabola with roots at $x = x_n$, and $x = x_{n+1}$ and slope $\pm 1/2$ at these points. On the other hand, the two-phase regions are expected to survive for small non-zero values of τ; the free energy for those regions remains a linear function of τ and $(\tau \cdot \partial x/\partial \mu)$ diverges. A typical zero-temperature form of the incremental capacity, with one- and two-phase intervals, is shown in Fig. 2 for $y = 1/3$, $1/3 < \psi_1 < 1/2$.

4. FINITE-TEMPERATURE RESULTS

The minimization of ω in Eq. (6) with respect to the $\{d_{\nu\sigma}\}$ yields the following expression after some simple algebraic manipulation:

$$d_{\nu\sigma} = \frac{p_\sigma}{\exp\{[\psi_\sigma + 3(3x-n_\nu) - \mu]/\tau\} + 1} \quad . \tag{9}$$

Thus, the occupation variables $d_{\nu\sigma}$ obey a Fermi-Dirac distribution, with the appropriate mean-field-approximation value $U[\psi_\sigma + 3(3x-n_\nu)]$ for the energy of an occupied site designated by the indices $\nu\sigma$. This type of Fermi-Dirac distribution can be easily understood, since each site of the lattice can be either empty or occupied by at most one particle.

Through a summation over the chemical types σ, the set of equations given by (9) is reducible to one equation of only one variable n_ν, with the input parameters $(9x-\mu)$, $\underline{y}$, τ and ψ_1. This equation has in general three roots. The variables n_ν, which satisfy $n_\alpha \geq n_\beta \geq n_\gamma$, can be assigned in principle in ten different ways (triplets) to the three roots. Comparison of the resulting grand potentials as functions of the chemical potentials for the ten triplets leads to phase diagrams as those shown in Fig. 3.

For $y = 1/2$, the phase diagram in the (x, τ) plane is symmetric about $x = 1/2$, for any value of the site energy parameter ψ_1. In Fig. 3, the order-disorder curves for the $\psi_1 = 1/4$ and 4 illustrate the additional disorder introduced into the system by the quenched random distribution of different species of host atoms. The main effect of a small finite ψ_1 is a quadratic decrease of the critical temperature for the mean-field order-disorder transition[3] at $x = 1/2$, from the value $\tau_c = 0.75$ at $\psi_1 = 0$. On the other hand, large values of ψ_1 lead to topologically different phase diagrams. Depending on the value of τ, we can have alternate intervals of order and disorder as $\underline{x}$ increases from 0 to 1. The critical temperature τ_c at $x = 1/2$ for $y = 1/2$ is plotted in Fig. 4 as a function of ψ_1. We see that τ_c drops from 3/4 at $\psi_1=0$ to 3/8 as $\psi_1 \to \infty$.

Simple physical interpretations can be given to features of incremental capacity curves obtained from the present model. We show in Fig. 5(a) the results for $y = 0.8$, $\psi_1 = 2$, $\tau = 0.4$. In this case, there is only one interval where spatially ordered phases are stable, between $x \approx 0.52$ and $x \approx 0.82$. The divergences at these points are due to order-disorder transitions. The two minima within the order interval are caused by the appearance of long-range ordered structures when sites of the highest-energy chemical type ($\sigma = 2$) are being filled. The other two minima or dimples, at values of $\underline{x}$ close to $(1-y)^2 = 0.04$ and $(1-y^2) = 0.36$ are caused by another type of ordering, associated with the nearly complete filling of the chemical types $\sigma = 0$ and 1.

Because it is a mean-field theory, the present model is expected to be more accurate when the correlations between sites are not important, i.e., in the spatially disordered phase. In fact we get better agreement with the experimental data for $Li_xTa_yTi_{1-y}S_2$ for $0.1 < y < 0.5$, where smooth incremental capacity curves obtained by Thompson[5] suggest a disordered distribution of Li ions. We show the results for $y = 0.3$ in Fig. 5(b), with our input parameters $\psi_1 = 3$, $\tau = 0.75$, together with Thompson's experimental data.

5. CONCLUSIONS

We have studied the influence of a quenched random distribution of different species of host atoms on the order-disorder phase diagram of the intercalate ions. The mean-field model for the spatially disordered phase gives a reasonable approximation for the incremental capacity curves of the Ti-rich end of the $Li_xTa_yTi_{1-y}S_2$ series. It is doubtful whether any rigid-lattice model can accurately describe the behavior on the Ta-rich end, where crystal distortions in the host play an important role.

Although the order-disorder phase diagrams are not expected to be accurate in the mean-field approximation, the present model results in interesting physical features, like the existence of minima in the incremental capacity due to two different kinds of ordering of the particles. There is a spatial ordering that results from filling the sublattices one by one, and a "chemical type" ordering that results from filling the sites with different chemical environment in the sequence of the values of their site energies. In addition, divergences of the incremental capacity can also be due to two distinct kinds of coexistence of phases: one occurring about an order-disorder transition, like in Fig. 5(a), and the other resulting from the coexistence of two ordered phases, like in Fig. 2.

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Table 1
Notation for the variables in Eq. (3).

	On sublattice ν	On chemical site of type σ	On chemical site of type σ, sublattice ν
Total number of sites	$\frac{N}{3}$	Np_σ	$\frac{N}{3} p_\sigma$
Number of occupied sites	$\frac{N}{3} n_\nu$	Nc_σ	$\frac{N}{3} d_{\nu\sigma}$

Figure 1

Ground-state mean-field phase diagrams in the (x, ψ_1) plane for the triangular lattice gas with three sublattices and three chemical types, for (a) $y = 1/3$ and (b) $y = 1/2$.

Figure 2

Zero-temperature limit of the reduced incremental capacity multiplied by reduced temperature $(\tau \cdot \partial x/\partial \mu)$ for $y = 1/3$, $1/3 < \psi_1 < 1/2$.

Figure 3

Phase diagrams in the (x, τ) plane with a site energy parameter $\psi_1 = 1/4$ and $\psi_1 = 4$ for $y = 1/2$. For each ψ_1, the disordered phase is stable above the upper curve and ordered phases occur below the lower curve; the narrow bands between the two curves are regions of order-disorder phase coexistence. An arrow indicates the critical temperature $\tau_c = 3/4$, the maximum τ (at $x = 1/2$) for similar curves with $\psi_1 = 0$.

Figure 4

Reduced critical temperature for the order-disorder transition at $x = 1/2$ for $y = 1/2$ as function of the site energy parameter ψ_1.

Figure 5

Reduced incremental capacity multiplied by reduced temperature for (a) $y = 0.8$, $\psi_1 = 2$, $\tau = 0.4$; (b) $y = 0.3$, $\psi_1 = 3$, $\tau = 0.75$. In (b) the circles are the experimental data of Thompson (ref. 5) for $Li_xTa_{0.3}Ti_{0.7}S_2$.

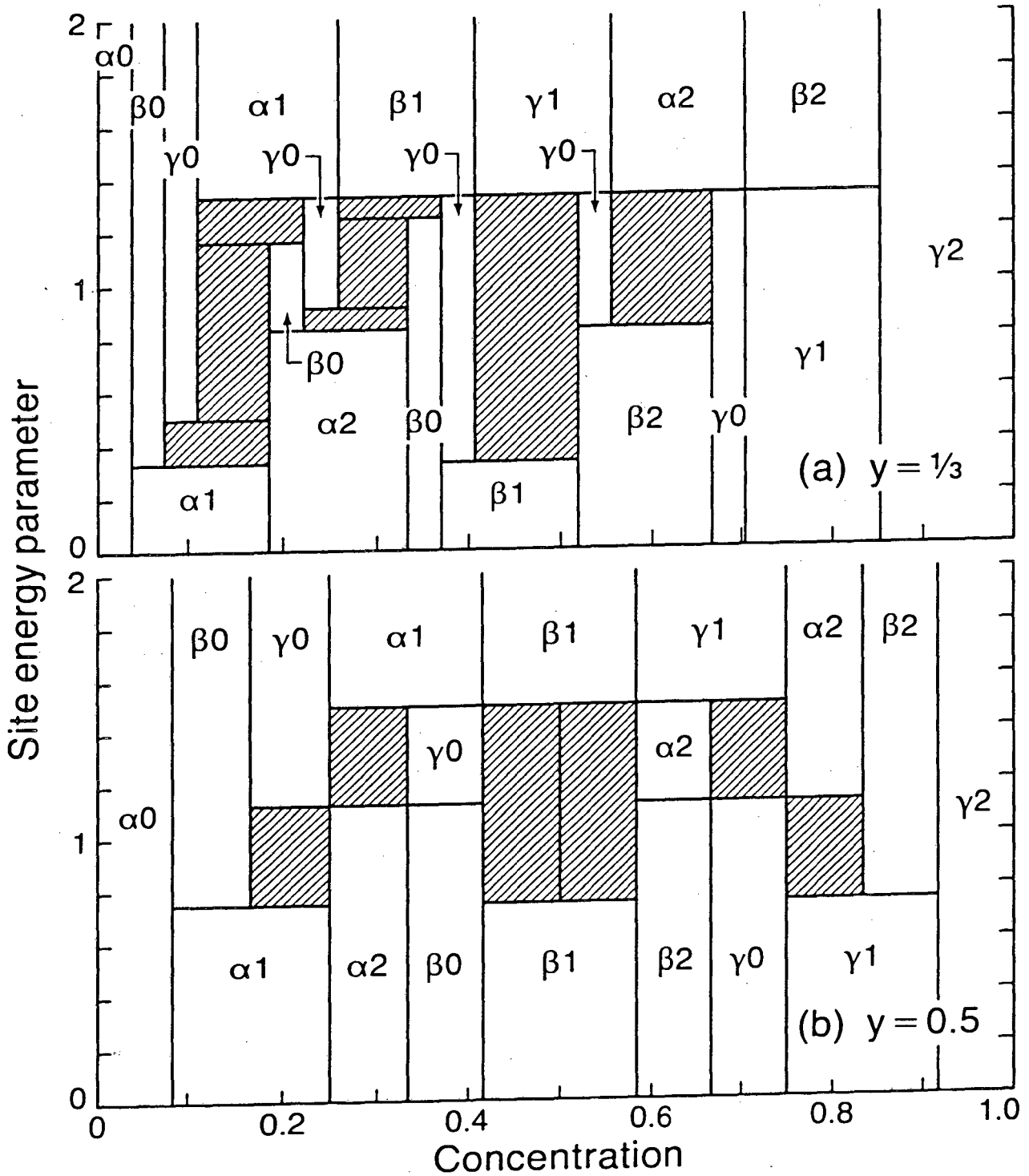
Site energy parameter
Concentration
(a) y = 1/3
(b) y = 0.5
α0
β0
γ0
α1
β1
γ1
α2
β2
γ2
0
1
2
0.2
0.4
0.6
0.8
1.0

Figure 1

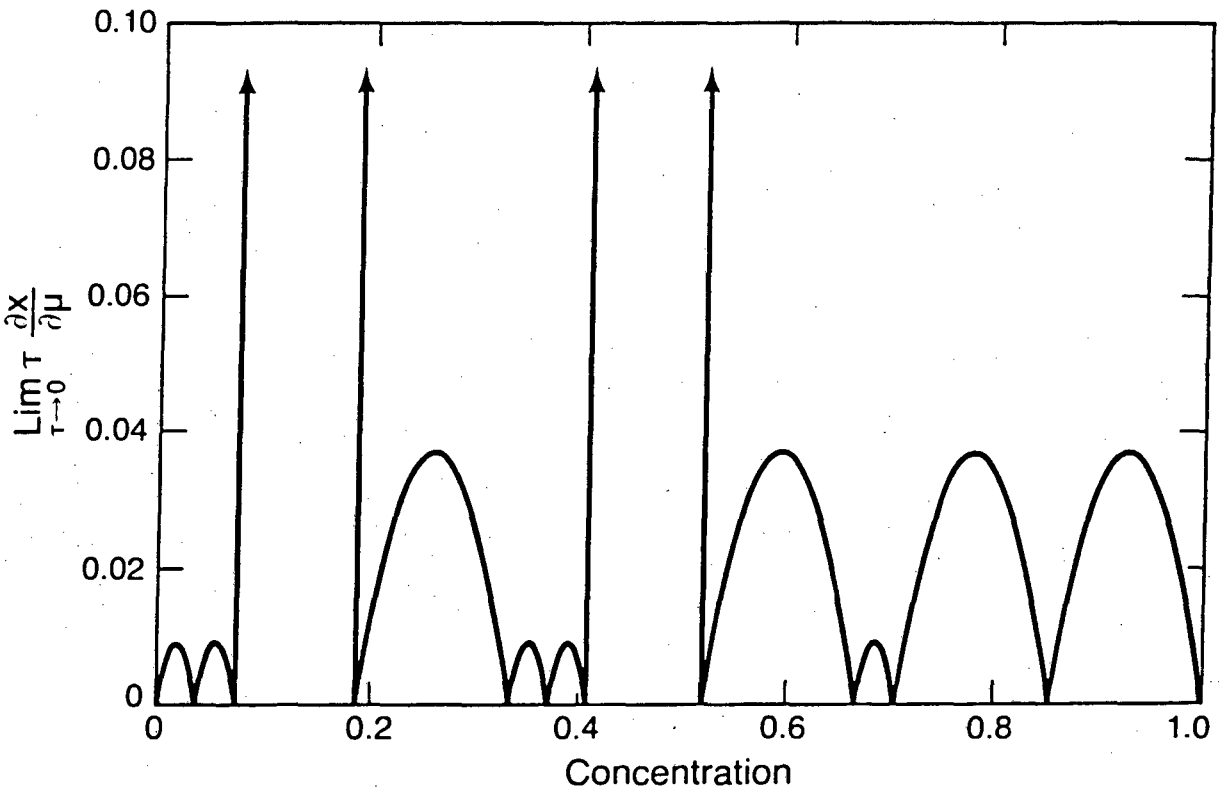
0.10
0.08
0.06
0.04
0.02
0
$\lim_{T \to 0} T \frac{\partial x}{\partial \mu}$
0
0.2
0.4
0.6
0.8
1.0
Concentration

Figure 2

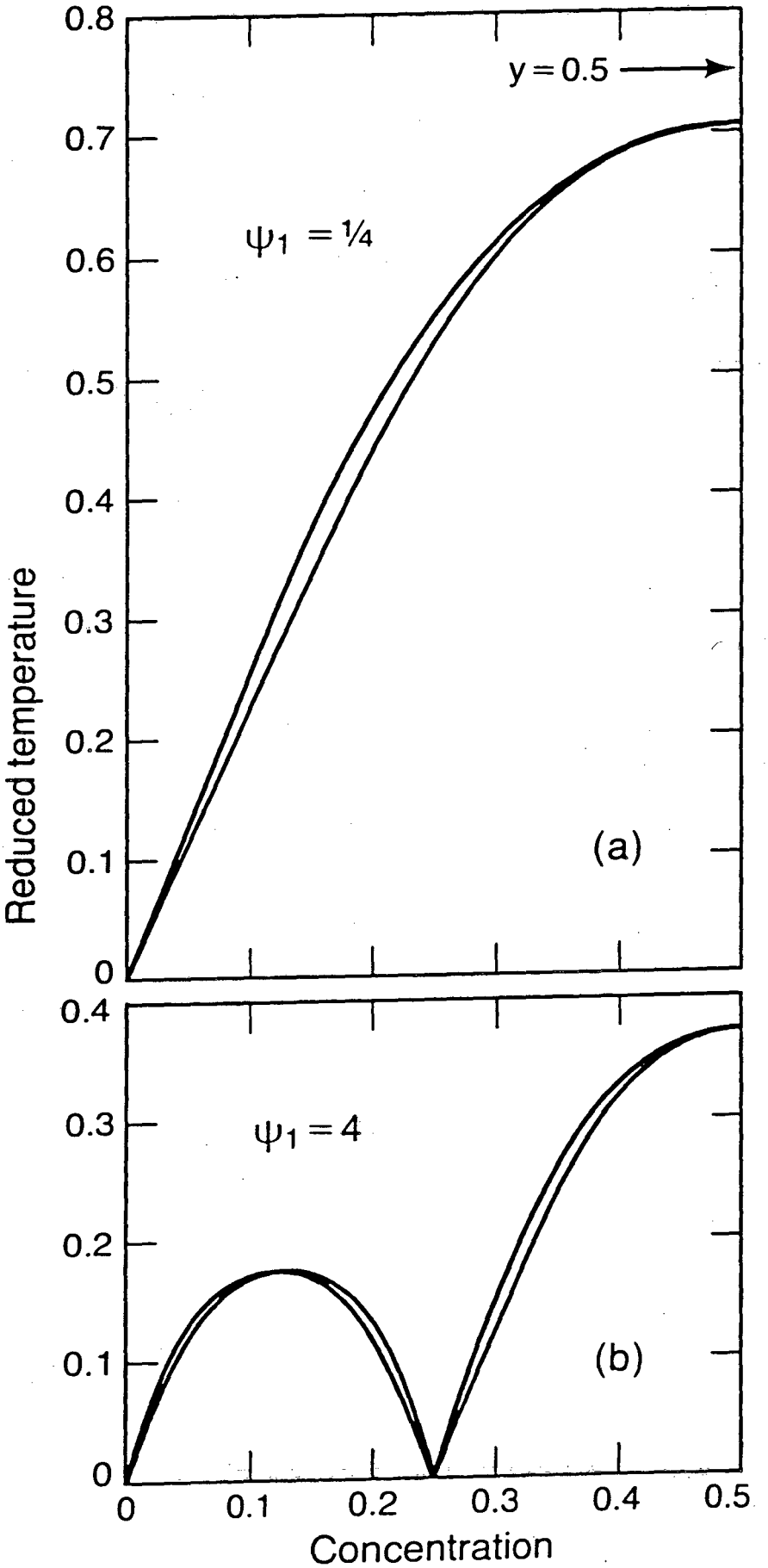
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
y = 0.5
ψ1 = ¼
(a)
Reduced temperature
0.4
0.3
0.2
0.1
0
ψ1 = 4
(b)
0
0.1
0.2
0.3
0.4
0.5
Concentration

Figure 3

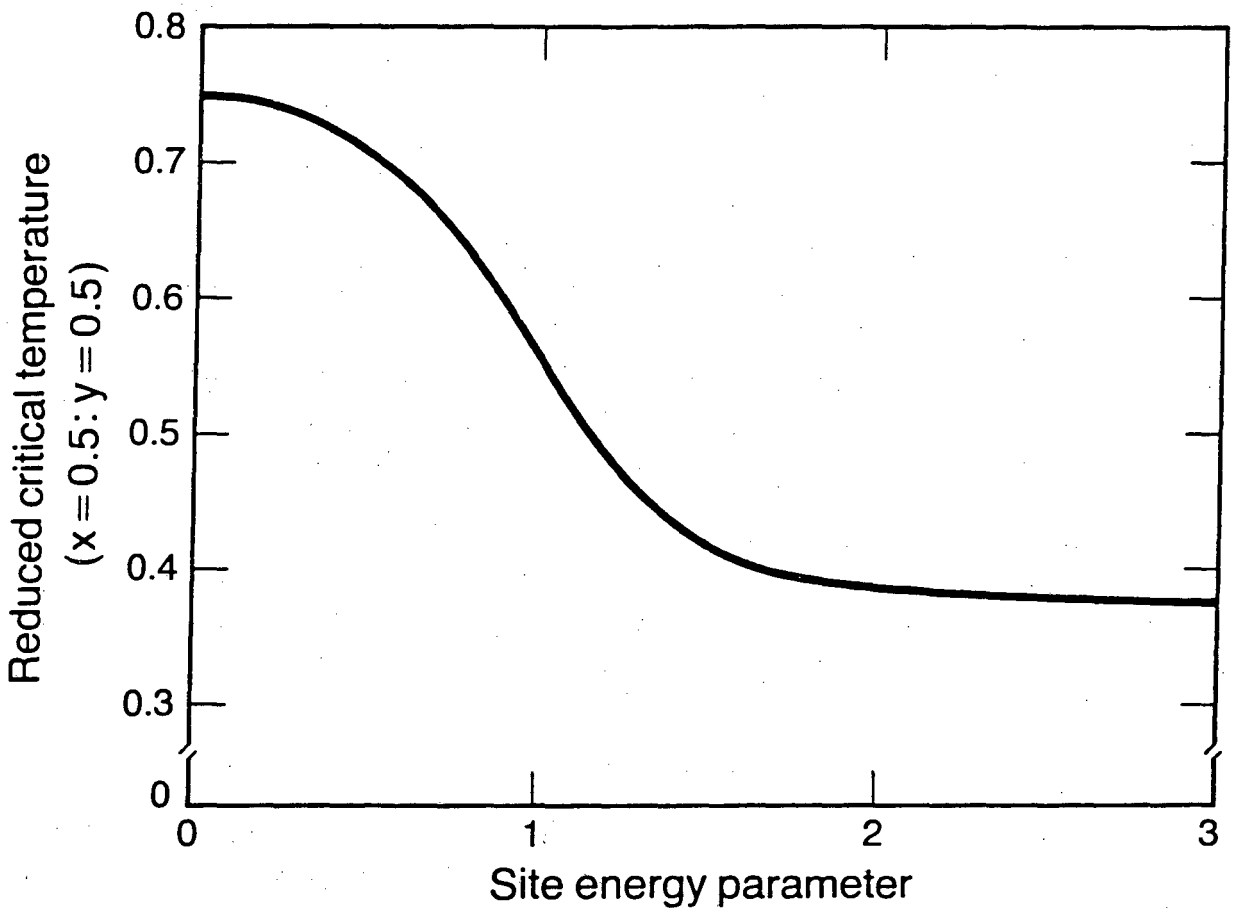
0.8
0.7
0.6
0.5
0.4
0.3
0
Reduced critical temperature
(x = 0.5: y = 0.5)
0
1
2
3
Site energy parameter

Figure 4

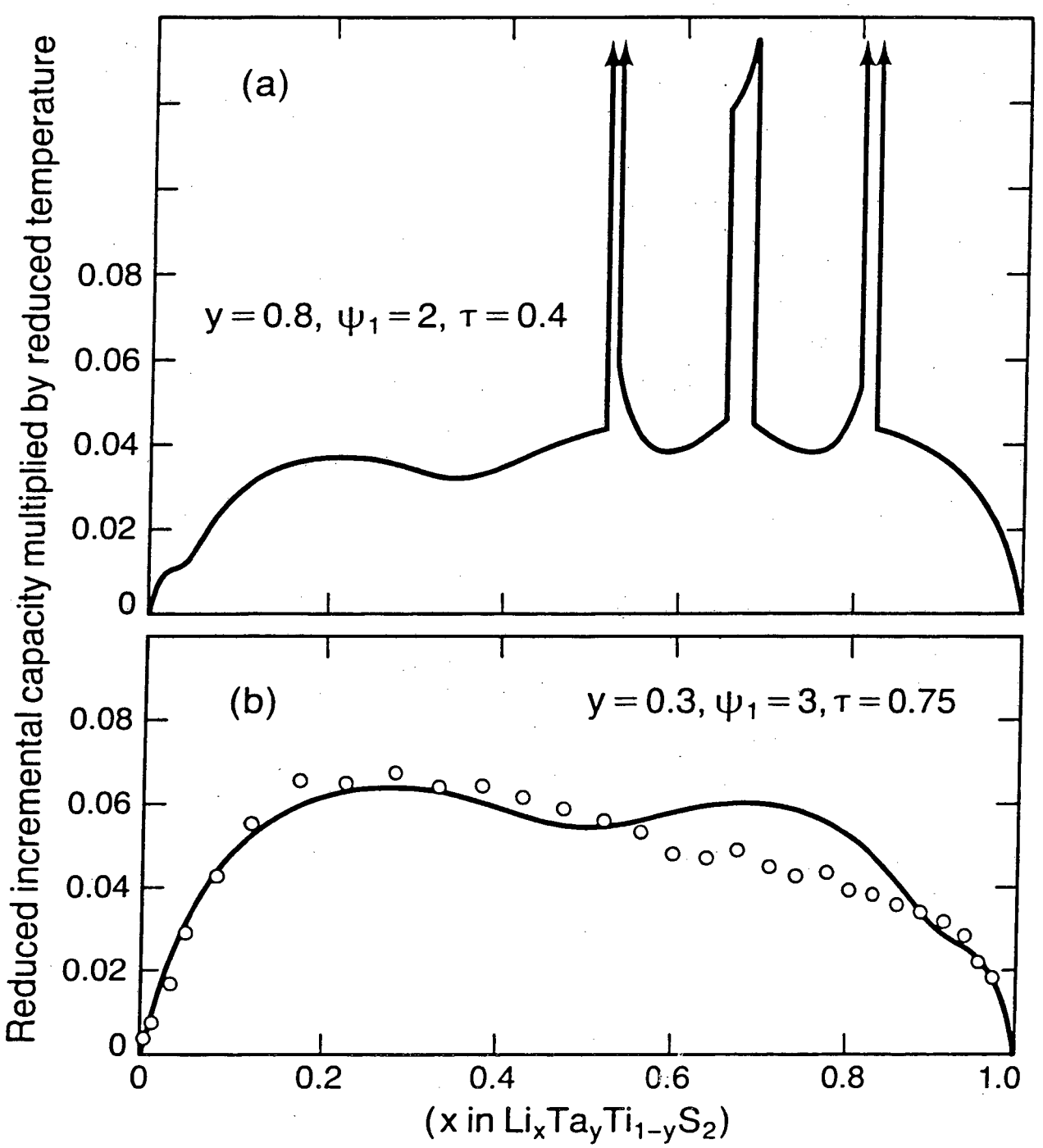
(a)
y = 0.8, ψ1 = 2, τ = 0.4
(b)
y = 0.3, ψ1 = 3, τ = 0.75
Reduced incremental capacity multiplied by reduced temperature
0.08
0.06
0.04
0.02
0
0
0.2
0.4
0.6
0.8
1.0
(x in LixTayTi1-yS2)

Figure 5

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