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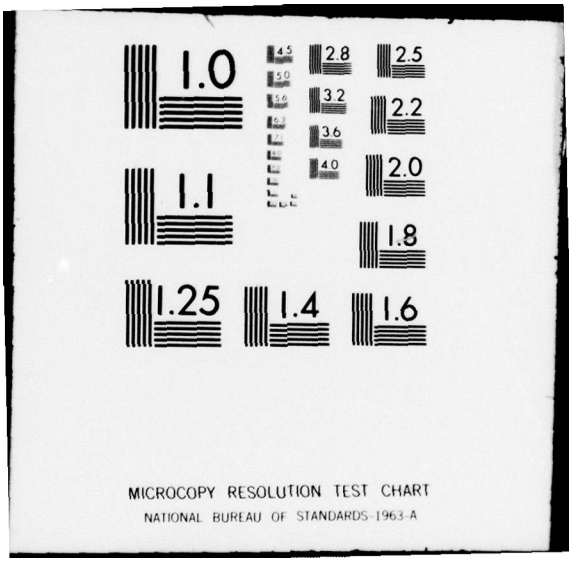
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ORDER-DISORDER TRANSFORMATIONS IN CHEMISORBED LAYERS: OXYGEN ON W(110).

by

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Order-Disorder Transformations in Chemisorbed Layers: Oxygen on W(110)

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Abstract

We have investigated the order-disorder transformation in oxygen adsorbed on W(110). An analysis of the ordering at T=0 using the lattice gas formalism shows that there must be significant three-particle interactions to break the particle-hole symmetry. This is necessary since there is a p(2x2) phase at three-quarter coverage which is not present at one-quarter coverage. Monte Carlo techniques are used to obtain estimates of the strength of the two and three-particle interactions by matching calculated and measured LEED intensity curves. The qualitative characteristics of the phase diagram are discussed with emphasis on the multicritical points which must be present if the transition at half coverage is second order. Evidence in support of a second order transition is reviewed.

I. Introduction

The development of low energy electron diffraction (LEED) techniques has led to many important discoveries in surface science. Recently, increasing attention has been paid to the study of order-disorder transformations in chemisorbed layers.[1-9] From measurements of the diffraction patterns it has been possible to infer the symmetry of the ordered phase as well as to obtain estimates of the size of the regions of coherent scattering,[10,11] The experimental investigations have led to a number of theoretical studies of order-disorder transformations in two dimensional systems in which numerical and analytic techniques have been employed.[10,12-16]

One of the more interesting of the order-disorder systems involves oxygen atoms adsorbed on the (110) face of tungsten (O/W(110)). Various LEED studies have established many of the features of the phase diagram.[6,8,9] The availability of data for the temperature dependence of the LEED intensities has stimulated numerical investigations of lattice gas models for the adsorbed layer.[17,18] The temperature dependence of the LEED intensity can be calculated numerically using Monte Carlo techniques.[10] By matching the calculated curves with experiment it has been possible to obtain estimates for the strengths of the two-particle interactions between the oxygen atoms.[17,18]

The theoretical studies of O/W(110) mentioned previously were limited to coverages θ in the interval $0 \leq \theta \leq 0.5$. In this paper we extend the analysis to the entire range $0 \leq \theta \leq 1$. Our main results pertain to the asymmetry of the phase diagram about half coverage. We show that to account for the asymmetry it is necessary to include significant three-particle

interactions in the lattice gas Hamiltonian. By fitting the LEED intensity curves we are able to obtain estimates for the strengths of these interactions. The second part of this study relates to the phase diagram. We outline the general features of the phase diagram in the temperature-chemical potential plane. Particular emphasis is placed on the multicritical points which must be present when the transition at half coverage is second order. Evidence in support of this interpretation is reviewed. The data are found to be compatible with a second order transition, but a weak first order transition can not be ruled out.

The remainder of the paper is divided into three sections. In Sec. II we analyze the asymmetry and its implications for the model Hamiltonian while in Sec. III we discuss the phase diagram. We comment on our findings in Sec. IV.

II. Asymmetry

LEED studies of O/W(110) have shown that at low coverages ($\theta < 0.35$) there is a first order phase boundary separating a disordered "gas" phase from a coexistence region consisting of "islands" of oxygen atoms ordered in a p(2x1) structure.[6,8,9] In the vicinity of $\theta = 0.35$ there is a jump in the transition temperature from 460K to 690K followed by a gradual increase to 720K at $\theta = 0.5$. Above half coverage there is evidence of a p(2x2) phase coexisting with the p(2x1) and disordered phases. Unfortunately, experimental studies in this region are handicapped by the difficulty of obtaining accurate estimates of the coverage.

The lattice gas calculations mentioned earlier (Refs. 17 and 18) involved model Hamiltonians with pairwise interactions as shown in Fig. 1, where we also indicate the arrangement of the atoms in the p(2x1) phase.

In the models studied there was an interaction ε_1 between nearest neighbors, ε_2 between second nearest neighbors, ε_3 between third nearest neighbors, and ε_4 between fifth nearest neighbors, which are in the same direction as the nearest neighbors. A reasonable fit to the data was obtained in Ref. 17 with the values ε_1 = -0.072 eV, ε_2 = 0.080 eV, and ε_3 = 0, and ε_4 = -0.049 eV. In Ref. 18 comparable fits were obtained with ε_1 = -0.09 eV $\varepsilon_2 = \varepsilon_3$ = 0.075 eV and ε_4 = -0.03 eV. Although it is clear that unique values for the ε_i can not be obtained in this way the Monte Carlo studies do provide semi-quantitative estimates of the interactions

As mentioned in Refs. 17 and 18 a lattice gas model with only pairwise interactions generates a phase diagram which is symmetric about half coverage when particles and vacancies are interchanged.[19] In order to break the particle-hole symmetry there must be three-particle (or, more generally, n-particle with n an odd integer) interactions in the Hamiltonian. Moreover, when the asymmetry is such that there are phases present at $\theta > 0.5$ which do not appear at less than half coverage (or vice versa), as is the case for O/W(110), it is often possible to obtain lower bounds on the strengths of the three-particle interactions from an analysis of the ordering at T=0.

The bounds on the three-particle interactions come from a study of the grand potential $\Omega(T,\mu) = U-TS-\mu N$, where U is the internal energy, T is the temperature, S is the entropy, μ is the chemical potential, and N is the number of atoms. Standard themodynamic arguments show that Ω is a minimum at equilibrium when the system is in contact with a reservoir which maintains it at constant T and μ.

In order to see the consequences of the minimization principle we consider model three-particle interactions of the form displayed in Fig. 2

where we also indicate the arrangement of the atoms in the p(2x2) phase. It should be emphasized that there are likely to be three-particle interactions other than those shown. However from arguments based on bond length we expect ε_{TP}^{a} and ε_{TP}^{b} to be the most important. With couplings as indicated in Figs. 1 and 2 the zero temperature limit of the grand potential per site of the fully occupied lattice (p(1x1)) is given by

$$\Omega_1(0,\mu) = 2\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + 2\varepsilon_4 + 4\bar{\varepsilon}_{TP} - \mu, \qquad (1)$$

where $\bar{\varepsilon}_{TP} = \frac{1}{2}(\varepsilon_{TP}^{a} + \varepsilon_{TP}^{b})$. Equation 5 is obtained by calculating n_i, number of interactions of type i. At zero temperature the entropy is zero while internal energy is given by the sum $\Sigma_i \alpha_i \varepsilon_i n_i$ where (to avoid double counting) $\alpha_i = 1/2$ and 1/3 for two-particle and three-particle interactions, respectively. The grand potential of the p(2x2) phase associated with three-quarter coverage takes the form

$$\Omega_{0.75}(0,\mu) = \varepsilon_1 + \frac{1}{2}\varepsilon_2 + \frac{1}{2}\varepsilon_3 + \frac{3}{2}\varepsilon_4 + \bar{\varepsilon}_{TP} - \frac{3}{4}\mu. \qquad (2)$$

The zero temperature limit of the grand potential of the p(2x1) phase is written

$$\Omega_{0.5}(0,\mu) = \frac{1}{2}\varepsilon_1 + \varepsilon_4 - \frac{1}{2}\mu, \qquad (3)$$

while the complementary p(2x2) phase at $\theta = 0.25$ has a grand potential given by

$$\Omega_{0.25}(0,\mu) = \frac{1}{2}\varepsilon_4 - \frac{1}{4}\mu\ . \qquad (4)$$

Finally, we note that the grand potential of the empty lattice $\Omega_0(0,\mu)$, is equal to zero.

At T=0 the boundary, μ_{12}, between the p(1x1) and p(2x2) phases is obtained by equating $\Omega_1(0,\mu)$ and $\Omega_{0.75}(0,\mu)$. We have

$$\mu_{12} = 4(\epsilon_1 + \tfrac{1}{2}\epsilon_2 + \tfrac{1}{2}\epsilon_3 + \tfrac{1}{2}\epsilon_4 + 3\bar{\epsilon}_{TP}). \quad (5)$$

Likewise, the boundary between the p(2x2) and p(2x1) phases, μ_{23}, follows from equating (3) and (4). We find

$$\mu_{23} = 4(\tfrac{1}{2}\epsilon_1 + \tfrac{1}{2}\epsilon_2 + \tfrac{1}{2}\epsilon_3 + \tfrac{1}{2}\epsilon_4 + \bar{\epsilon}_{TP}) \quad (6)$$

Finally, the boundary between the p(2x1) phase and the empty lattice, μ_{34}, which follows from equating $\Omega_{0.5}(0,\mu)$ and $\Omega_0(0,\mu)$, is given by

$$\mu_{34} = \epsilon_1 + 2\epsilon_4 \quad (7)$$

Assuming there are no phases other than those so far observed the phase diagram of O/W(110) in the zero temperature limit will consist of a p(1x1) phase at $\theta = 1$, a p(1x1) and p(2x2) coexistence region for $0.75 < \theta < 1$, a p(2x2) phase at $\theta = 0.75$, a p(2x2) and p(2x1) coexistence region for $0.5 < \theta < 0.75$, a p(2x1) phase at $\theta = 0.5$ and a p(2x1) and empty lattice coexistence region (i.e. p(2x1) islands) for $0 < \theta < 0.5$. This particular sequence of phases requires $\mu_{12} > \mu_{23} > \mu_{34}$. In addition, it is necessary that the postulated phases have a grand potential which is lower than the grand potentials of the other phases.

At T=0 the grand potentials of the different phases, $\Omega_\theta(0,\mu)$, are linear functions of μ with slope equal to $-\theta$, as shown in Fig. 3. Because of the difference in slopes, if $\mu_{12} > \mu_{23} > \mu_{34}$ we will have $\Omega_1(0,\mu) < \Omega_{0.75}(0,\mu)$, $\Omega_{0.5}(0,\mu)$, $\Omega_0(0,\mu)$ for $\mu > \mu_{12}$; $\Omega_{0.75}(0,\mu) < \Omega_1(0,\mu)$, $\Omega_{0.5}(0,\mu)$, $\Omega_0(0,\mu)$ for $\mu_{23} < \mu < \mu_{12}$; $\Omega_{0.5}(0,\mu) < \Omega_1(0,\mu)$, $\Omega_{0.75}(0,\mu)$, $\Omega_0(0,\mu)$ for $\mu_{34} < \mu < \mu_{23}$; and $\Omega_0(0,\mu) < \Omega_1(0,\mu)$, $\Omega_{0.75}(0,\mu)$, $\Omega_{0.5}(0,\mu)$ for $\mu < \mu_{34}$. The absence of the p(2x2) phase at one-quarter coverage will be ensured if in addition we have $\Omega_{0.5}(0,\mu_{34}) < \Omega_{0.25}(0,\mu_{34})$.

The inequalities for the chemical potentials lead to the equations

$$\varepsilon_1 + 4\bar{\varepsilon}_{TP} > 0, \tag{8}$$

coming from $\mu_{12} > \mu_{23}$, and

$$\varepsilon_1 + 2\varepsilon_2 + 2\varepsilon_3 + 4\bar{\varepsilon}_{TP} > 0, \tag{9}$$

coming from $\mu_{23} > \mu_{34}$. The inequality for the grand potential, $\Omega_{0.5}(0,\mu_{34}) < \Omega_{0.25}(0,\mu_{34})$, will be satisfied if we also have

$$\varepsilon_1 < 0. \tag{10}$$

Equation (10) indicates that there must be an attractive interaction between nearest neighbors. From Eq. (8) we infer that there must also be a repulsive three-particle interaction with $\bar{\varepsilon}_{TP} > -\varepsilon_1/4$. From Eq. (9) we see that $\varepsilon_2 + \varepsilon_3$ can be negative but not less than $-\frac{1}{2}(\varepsilon_1 + 4\bar{\varepsilon}_{TP})$.

We have carried out a series of Monte Carlo calculations with both two-particle and three-particle interactions. The former were constrained by the conditions $\varepsilon_1 = -0.072$ eV, $\varepsilon_3 = 0$, and $\varepsilon_4 = -0.049$ eV (the values inferred in Ref. 17 assuming only two-particle interactions), while ε_2, ε_{TP}^a, and ε_{TP}^b were varied in such a way as to reproduce the temperature dependence of the normalized intensities of the LEED patterns at $\theta = 0.25$, $\theta = 0.5$, and $\theta = 0.75$. Reasonable fits were obtained with $\varepsilon_2 = 0.056$ eV and $\varepsilon_{TP}^a = \varepsilon_{TP}^b = 0.052$ eV, the former value being only slightly smaller than the estimate $\varepsilon_2 = 0.080$ eV obtained with $\varepsilon_{TP}^{a,b} = 0$.[17] On the basis of the Monte Carlo calculations we have concluded that our model three-particle interactions have only a small effect on the LEED intensity for $\theta < 0.5$, but become increasingly important at higher coverages.

The analysis in this section has been limited to zero temperature. We postpone comment on the significance of our results until after a discussion of the phase diagram at finite temperatures.

III. Phase Boundaries

In this section we consider the phase diagram of O/W(110). Since there is insufficient experimental information to establish the location of the boundaries over the entire range of coverage we will confine our discussion to the general features of the diagram. Such an analysis is most easily carried out in the μ-T plane where the phase diagram has the form shown schematically in Fig. 4. A fundamental problem relating to the diagram involves the nature of the phase transitions associated with various segments of the boundary. From group theoretic arguments, i.e. Landau rules,[12,13] we conclude that the boundary of the p(2x2) phase, EDF, must be lines of first order transitions. As in the familiar liquid-vapor system the lines of first order transitions open into two-phase coexistence regions when the corresponding diagram is plotted in the θ-T plane. Exceptions to this can occur at special values of θ which represent saturation coverages for one or the other of the phases (e.g. $\theta = 0.5$ for the p(2x1) phase). For these values of θ there is no coexistence region so that the order parameter associated with the saturated phase changes discontinuously at the boundary when the transition is first order.

The interesting segment is ABCD, the boundary between the p(2x1) phase and the disordered phase. Experimental evidence mentioned earlier[8,9] indicates that at low coverages there is a two-phase coexistence region below 460K. The coexistence of the p(2x1) and disordered phases means that at least part of ABCD is a line of first order transitions. The question then arises as to whether the first order line extends all the way to D or terminates at B. If the latter is the case, which is allowed by symmetry,[12,13] then there are two possibilities: either the line of second order transitions extends only from B to C and the segment CD is a line of first order transitions or the segment BCD is entirely second order. (More than one second order segment is also possible but seems unlikely.) As will be discussed in more detail below the

experimental data are compatible with there being a line of second order transitions. However there is insufficient evidence to come to any conclusions about the nature of the transitions along the segment CD.

When there is a line of second order transitions which changes into a first order line the end points of the second order line are multicritical points.[20] If only the segment BC is a second order line then points B and C are tricritical points or critical end points.[21] (Fourth order critical points[21] are also allowed.) Although it can not be completely ruled out on the basis of available experimental evidence the existence of critical end points appears to be unlikely. A critical end point, where the second order line intersects the boundary of the coexistence region in the θ-T plane at an arbitrary point, implies the coexistence of two distinct p(2x1) phases of different density as well as a bicritical end point.[21] Such features have not been observed.

If the segment BCD is a second order line then the point C has no special significance. However the point D, instead of being a triple point, is now a critical or tricritical end point, the latter being associated with the coalescing of the p(2x1) phase and the disordered phase in coexistence with the p(2x2) phase.[20]

The evidence in support of a second order segment comes from a study of the phase transition at half coverage. Were the transition at this coverage first order the intensity of the LEED pattern associated with the p(2x1) ordering would drop discontinuously to zero at the transition temperature. As is apparent from the data from Ref. 8, which is reproduced in Fig. 5, no such discontinuity is observed. However we can not rule out a small discontinuity which is obscured by rounding.

The rounding itself is an interesting phenomenon. We attribute at least part of it to finite size effects. As a result of surface inhomogeneities the oxygen layer is divided into a large number of quasi-independent thermodynamic subsystems. In order to obtain a lower estimate of the

characteristic size of these subsystems we haye carried out a series of Monte Carlo calculations with different size arrays. Our results are shown in Fig. 5 where we plot experimental data at half coverage and Monte Carlo data for 30x30, 20x20, and 10x10 arrays with periodic boundary conditions. From this figure we conclude that the observed intensity curves are consistent with a rounded second order transition involving subsystems with at least 10^2 - 10^3 sites. In connection with this point it should be mentioned that the minimum size of the thermodynamic subsystems is approximately the same as the mean size of the regions of coherent scattering which is inferred from the width of the diffraction spots at half coverage.[11]

IV. Discussion

A number of conclusions can be drawn from the theoretical studies of the order-disorder transformation in O/W(110). First, in order to reproduce the transitions with a lattice gas model it is necessary to have attractive interactions between nearest neighbors as well as attractive and repulsive interactions involving more distant neighbors. Second, the appearance of the p(2x2) phase when $\theta > 0.5$ implies the presence of significant repulsive three-particle interactions in the lattice gas Hamiltonian. Third, the most important two and three-particle interactions have strengths per particle on the order of 0.015 - 0.04 eV. The existence of indirect three-particle interactions in model systems has been discussed before.[22,23] To the best of our knowledge our results provide the first (albeit crude) quantitative estimates of three-particle interactions in a real chemisorbed system. However it should be noted that the estimates of the relative importantance of the two and three particle interactions inferred in Ref. 23 on the basis of model calculations are in qualitative agreement with our own findings.

Concerning the phase diagram we note that if there is a segment of the p(2x1)-disorder phase boundary which is a line of second order transitions, a result consistent with the Monte Carlo analysis and compatible with the experimental data at half coverage, then there are at least two multicritical points in the phase diagram. It should be emphasized that the arguments about the character of phase boundaries do not depend on the applicability of the lattice gas model but are a consequence only of the interplay of symmetry and thermodynamics.

Because of the complexity of the lattice gas Hamiltonian we are not optimistic about obtaining definitive values for the interactions using Monte Carlo techniques. Moreover numerical attempts to map out phase boundaries in the θ-T plane are prohibitively expensive. However additional experimental studies focusing on the existence, location, and character of the multicritical points would be of considerable interest.

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Captions

Fig. 1. Two-particle interactions, $\varepsilon_1,\ldots,\varepsilon_4$. The arrangement of particles (solid circles) and vacancies (open circles) characterizes the p(2x1) phase.

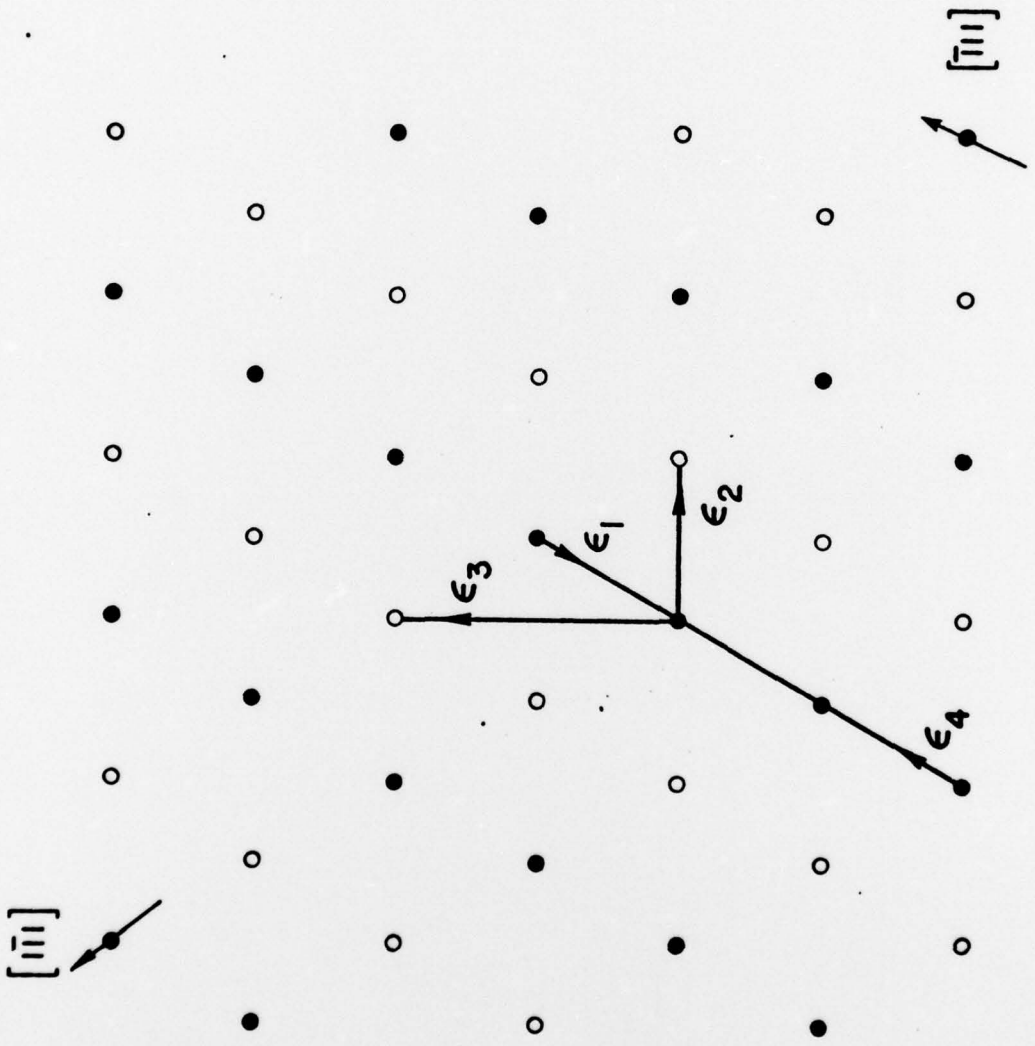
Fig. 2. Three-particle interactions. The triangles indicate the three-particle interactions used in the calculations. The arrangement of particles (solid circles) and vacancies (open circles) characterizes the p(2x2) phase.

Fig. 3. Grand potential vs. μ at T=0 (schematic). The grand potentials of the phases discussed in Sec. II are denoted by $\Omega_\theta\ (0,\mu)$, θ = 1, 0.75, 0.5, 0.25, 0. The point μ_{12} denotes the boundary between the p(1x1) and p(2x2) (θ=0.75) phases, μ_{23} is the boundary between the p(2x2) (θ=0.75) and p(2x1) phases, and μ_{34} is the boundary between the p(2x1) phase and the empty lattice.

Fig. 4. Oxygen on W(110) schematic phase diagram, μ-T plane. The points μ_{12}, μ_{23}, and μ_{34} mark the boundaries along the chemical potential axis (see Fig. 3). The points A,...,F are discussed in Sec. III. Note that first order lines in the μ-T plane become coexistence regions in the corresponding phase diagram in the θ-T plane.

Fig. 5. Normalized intensity of the p(2x1) LEED pattern vs. temperature at θ=0.5. Solid curve, experiment; O, 30x30 Monte Carlo results with periodic boundary conditions; × 20x20 Monte Carlo results with periodic boundary conditions; Δ, 10x10 Monte Carlo results with periodic boundary conditions. Dashed, chain and dotted curves have been drawn through the 30x30, 20x20 and 10x10 Monte Carlo data as a guide to the eye. The experimental

data are from Ref. 8. The Monte Carlo data were obtained with interaction parameters ε_1 = -0.072 eV; ε_2 = 0.056 eV, ε_3 = 0, ε_4 = -0.049 eV and $\varepsilon_{TP}^{a} = \varepsilon_{TP}^{b}$ = 0.052 eV.



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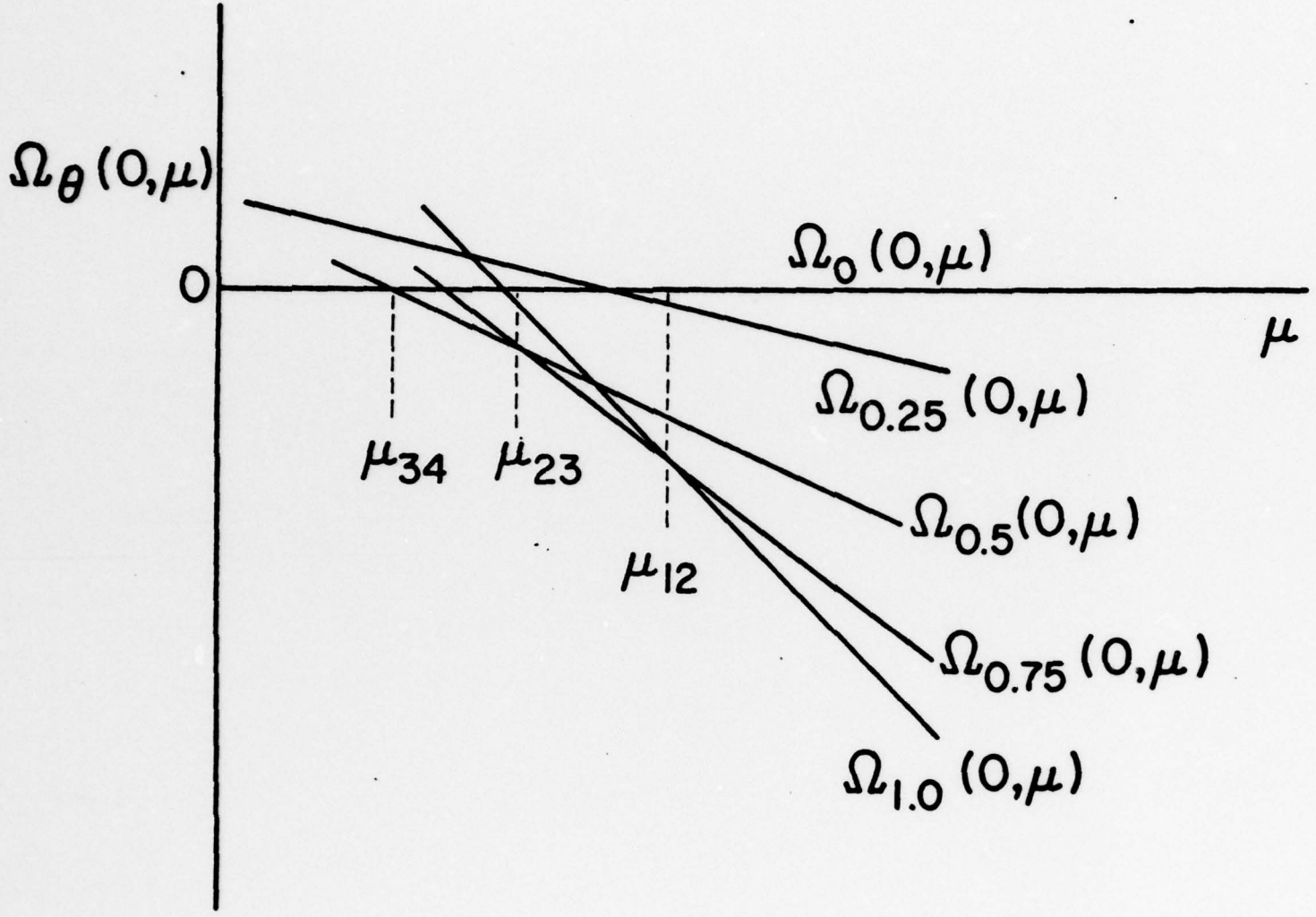
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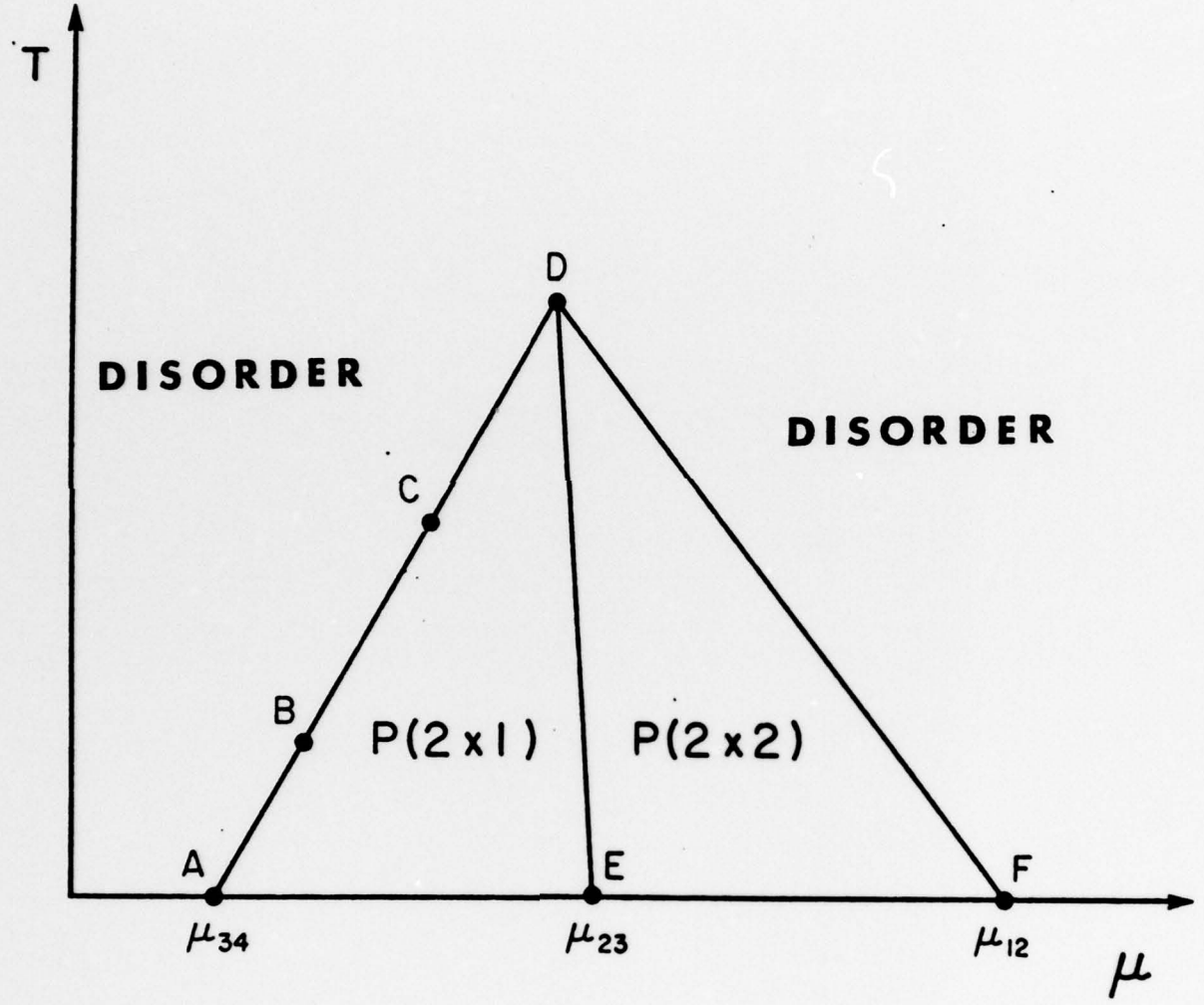
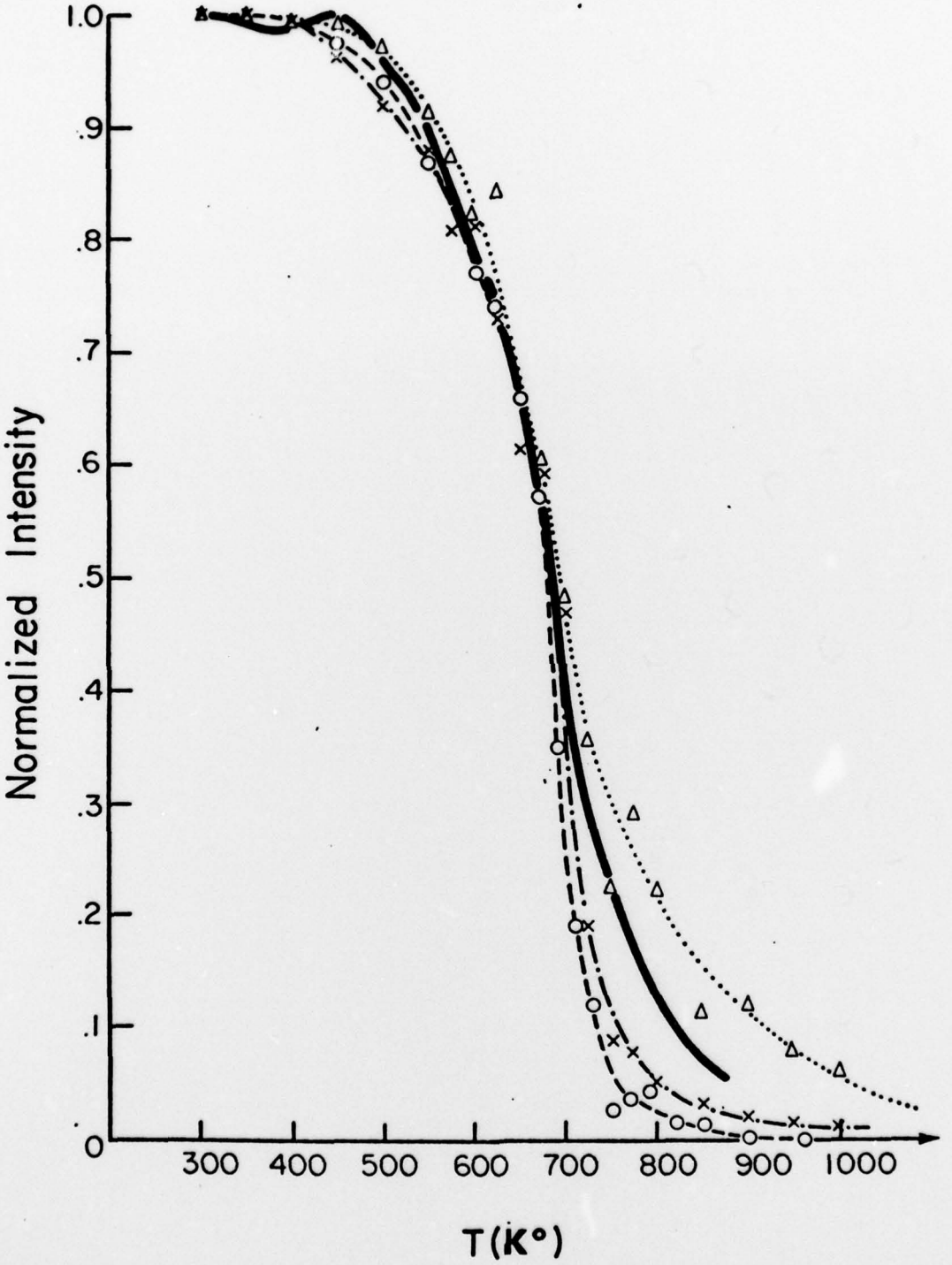
Fig. 3

Fig. 4

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300
400
500
600
700
800
900
1000
T(K°)

Fig. 5.