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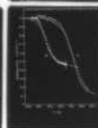
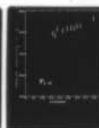
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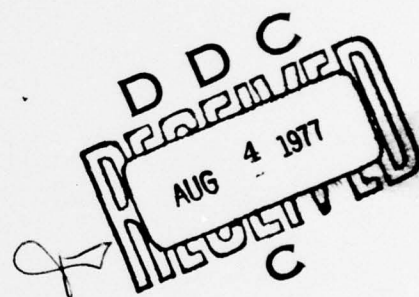
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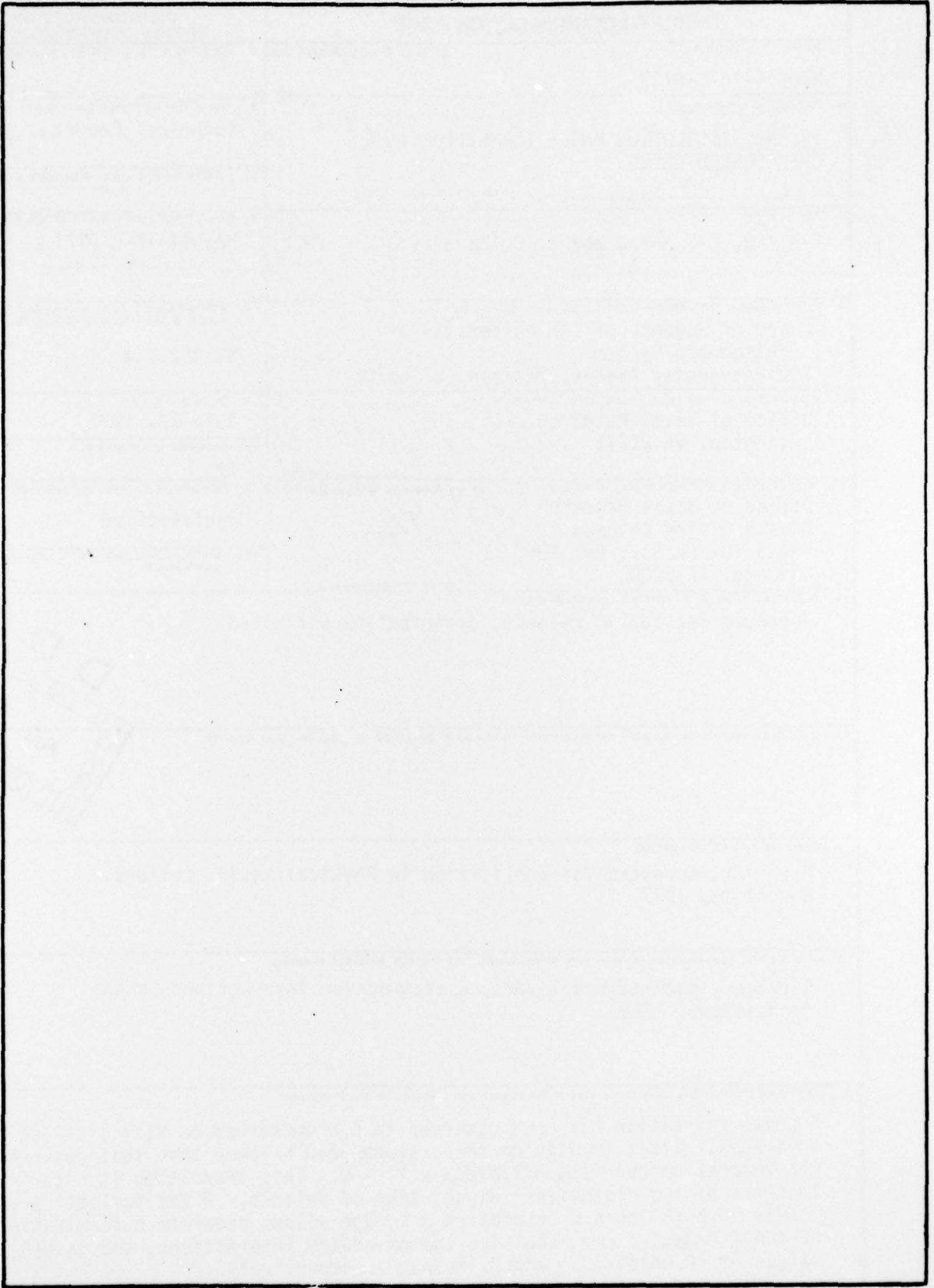
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ISLAND-DISSOLUTION PHASE TRANSITION IN A CHEMISORBED LAYER*

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A phase transition has been observed in O chemisorbed on W(110) at low coverages, with a transition temperature $\sim 250^\circ\text{K}$ lower than that observed for saturation coverage $\text{W}(110)\text{p}(2 \times 1) - \text{O}$. This transition is interpreted in terms of two-dimensional dissolution of islands. A fit to lattice gas models for both low and saturation coverage allows separate determination of the attractive and repulsive adatom-adatom interactions, and gives values of -0.069eV/atom and 0.15eV/atom respectively.

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The study of phase changes in overlayers is an important tool in understanding the interactions that adatoms undergo.⁽¹⁾ Very little work has been done on chemisorption systems, and only H/W(100)⁽²⁾ and O/W(110)⁽³⁾ have been studied in any detail. This Letter reports a new phase transition for O/W(110) at low coverages. We observe what we believe to be two-dimensional dissolution of the chemisorbed islands previously identified in this system^(3,4). As a result, we are able to determine separately attractive and repulsive adatom-adatom interaction energies leading to the $p(2 \times 1)$ structure.

The experiment⁽³⁾ consists of measuring the superlattice beam intensities and angular profiles in low-energy electron diffraction (LEED) from the W(110) surface covered with varying amounts of oxygen. The most important feature of this system is that the ordered overlayer forms by an island growth mechanism. This is established by the observation that superlattice LEED beams form already at very low coverage⁽⁴⁾. It implies a net attractive adatom-adatom interaction. However, the $p(2 \times 1)$ structure that is formed, shown in Fig. 1 and consisting of doubly spaced close-packed rows parallel to $\langle 111 \rangle$ directions, requires a nearest-neighbor repulsion. Streaking of spots is not observed in the diffraction pattern during formation of the overlayer^(3,4a,5). This implies that island formation is preferred over the formation of long rows, and therefore that the attractive interactions along $\langle 111 \rangle$ directions are about equal in magnitude^(5,6) and considerably smaller than the nearest-neighbor repulsion that prevents close packing.

Oxygen coverage determinations were made by establishing saturation coverage for the $p(2 \times 1)$ structure on the basis of maximum superlattice beam

intensity and using sticking coefficient measurements⁽⁷⁾ to relate exposure time to relative coverage. The temperature dependence of superlattice beams at a given coverage was then measured for various diffraction geometries. In each case the data plotted on a $\ln I$ vs T graph consist of a region of constant slope proportional to the Debye-Waller factor for thermal vibrations in the direction of the diffraction vector, and a sudden falloff away from this line. Figure 2 shows examples of this falloff (with the Debye-Waller contribution subtracted), for a low coverage of oxygen and for the $p(2 \times 1)$ saturation coverage. At the low coverage, the superlattice beam intensity begins to decay at a much lower temperature. Figure 3 shows the transition temperature T_t as a function of coverage, where T_t is chosen as the inflection point in the curves of Fig. 2. Clearly there are two transitions, one operative at low coverage, the other for saturation. In the intermediate-coverage region, both transitions are seen, the lower-coverage one becoming weaker as the coverage increases, but remaining at the same T_t .

We have interpreted the low-coverage transition as the dissolution of ordered regions, with atoms leaving the ordered regions and distributing themselves randomly on sites in the "sea" or uncovered part of the W substrate. To do this, only the attractive interaction leading to formation of ordered regions needs to be overcome, and in that sense the transition is similar to the sublimation of a solid or dissolution of a solute into solvent and fundamentally different from the saturation-coverage transition, where disordering can occur only by atoms moving into the more strongly repulsive nearest-neighbor sites. The latter thus corresponds to a true order-disorder transition, with a higher transition temperature, as shown in Fig. 3.

Since the dissolution and order-disorder transition temperatures are respectively a measure of the attractive interaction leading to island formation and the repulsive interaction preventing close packing, it now becomes possible to determine these interactions separately by first fitting the low-coverage transition and then using the resulting attractive interaction to fit the saturation - coverage transition and obtain the repulsive interaction. Because of the overlayer symmetry, one assumption is still necessary, i.e. that the attractive interactions - ϵ_a and - ϵ_{2b} (see Fig. 1) are equal.^(5,6)

To model the low-coverage transition, we consider the dissolution of islands consisting of an r-sublattice on which all sites are occupied and an s-sublattice on which all sites are empty⁽⁸⁾. As the temperature increases, the total number of atoms in the island, and thus participating in the diffraction, changes. Hence this is a problem in the grand canonical ensemble, and the lattice gas model developed by Lee and Yang⁽⁹⁾ gives a satisfactory description of the system. The present phase transition then is the two-dimensional analog of the condensation problem, to which the Lee and Yang model⁽⁹⁾ has been successfully applied^(10,11). Defining $b_{n_1 n_2} = 1$ if an r-sublattice site in the island is occupied, and $b_{n_1 n_2} = 0$ if an r-sublattice site is empty, or for any site in the sea, correspondence can be made to the ferromagnetic model for the spin system in zero external magnetic field⁽¹⁰⁾ by setting

$$\sigma_{n_1 n_2} = 2b_{n_1 n_2} - 1 = \begin{cases} 1 & \text{if an r-sublattice is occupied} \\ -1 & \text{if an r-sublattice is empty} \end{cases} \quad (1)$$

and

$$-4J \rightarrow -\epsilon_a = -\epsilon_{2b} \quad , \quad (2)$$

where n_1, n_2 are integers to indicate lattice positions, $\sigma_{n_1 n_2}$ is the spin operator for site $(n_1 n_2)$ and $-J$ is the usual nearest-neighbor attractive spin-spin interaction energy in the Ising model. Then

$$\langle b_{n_1 n_2} b_{n'_1 n'_2} \rangle = 1/4 [\langle \sigma_{n_1 n_2} \sigma_{n'_1 n'_2} \rangle + \langle \sigma_{n_1 n_2} \rangle + \langle \sigma_{n'_1 n'_2} \rangle + 1] \quad (3)$$

is the pair correlation function with $\langle \sigma_{n_1 n_2} \sigma_{n'_1 n'_2} \rangle$ the usual spin-spin correlation function and $\langle \sigma_{n_1 n_2} \rangle$ the average magnetization in the spin system.

As is well known, the angular distribution of intensity in any diffraction experiment is a measure of the pair correlation function⁽¹²⁾, the two being related by a Fourier transform. In our case the LEED superlattice reflections are a result of the new periodicity introduced by the ordered regions of O atoms. Hence the angular distribution of intensity in these beams is a measure of the overlayer pair correlation function. Evaluating this at the diffraction maximum gives for the maximum LEED intensity scattered by the overlayer

$$I_{\max}(T) = \sum_{n_1 n_2}^{A_c} \sum_{n'_1 n'_2}^{A_c} \langle b_{n_1 n_2}(T) b_{n'_1 n'_2}(T) \rangle f_1 f_2, \quad (4)$$

where the f 's are structure factors that are functions of the adsorbed layer island size and take into account the effects of boundaries on the diffracted intensity, and A_c is the coherence area of the instrument.

We have calculated the correlation functions of Eq. (3) for different $\epsilon_a = \epsilon_{2b}$, have evaluated $I_{\max}(T)$ through Eq. (4), and then compared with experimental $I_{\max}(T)$ curves. A typical fit is shown in Fig. 2a. The detailed shape of the model intensity decay with temperature depends both on the correlation functions and the f_i 's of Eq. (4), but ϵ_a does not. For arbitrary

finite lattice size, the correlation functions are very complicated and no analytic forms are known⁽¹³⁾. We have estimated these functions using the Onsager solutions⁽¹⁴⁾ for an infinite two-dimensional lattice. Details of this are presented elsewhere⁽¹⁵⁾. The f_i 's in Eq. (4) are the most important quantity in determining the shape of $I_{\max}^o(T)$. An experimentally determined⁽⁶⁾ $\sim 35\text{\AA}$ dia mean island size was used to fit the curves. Fits to the shape of $I_{\max}^o(T)$ with assumed 50% greater or lesser island sizes were much poorer.

The interaction energy ϵ_a was determined from the Onsager relation⁽¹⁴⁾

$$\sinh \frac{2 E_1}{k_B T_t} \sinh \frac{2 E_2}{k_B T_t} = 1, \quad (5)$$

where here $E_1=E_2=1/4 \epsilon_a$. A fit to the experimental transition temperature of 460°K gives $\epsilon_a=\epsilon_{2b}=0.069 \text{ eV/atom}$. As expected from Eq. (5) the determined value of ϵ_a is a quite sensitive function of T_t .

This value for the attractive interaction can now be used to analyze the second phase transition, for the saturation $p(2 \times 1)$ coverage, $T_t = 718^\circ\text{K}$. No further assumptions are necessary to extract the repulsive interaction that prevents the formation of a close packed structure. However, for this phase transition, a different model is required than for the dissolution transition, because the number of atoms participating in the diffraction is now constant. The model we use to describe it is a generalization of a model⁽²⁾ considering isotropic n.-n. interactions only. In our case anisotropic n.-n. interactions $-\epsilon_a$ and $+\epsilon_b$ are required. This is equivalent to a ferromagnetic system in zero magnetic field with attractive n.-n. interactions $-J_a$ and $-J_b$ if the following correspondence is made:

$$-4J_{\underline{a}} \rightarrow -\epsilon_{\underline{a}}, \quad -4J_{\underline{b}} \rightarrow -\epsilon_{\underline{b}} \quad . \quad (6)$$

With this generalization, we use the model of Ref. 2 to calculate again the correlation functions and $I_{\max}(T)$, the maximum intensity of the superlattice reflection as a function of T , in similar fashion as we did earlier for the dissolution phase transition. We fit the experimental $I_{\max}(T)$ curves for the saturation $p(2 \times 1)$ coverage by calculating correlation functions for different $\epsilon_{\underline{b}}$ using $\epsilon_{\underline{a}}$ from our earlier results. As before the transition temperature is defined through Eq. (5). This gives $\epsilon_{\underline{b}} = 0.15$ eV/atom. This value lies between that obtained by a more approximate model⁽²⁾ and that obtained by an assumed interaction strength in a Monte-Carlo calculation^(5,16).

It seems evident that dissolution transitions should be observable for other island-forming adsorbates. Since the fit of the above models to T_t does not depend critically on instrument response or island size, it should be straightforward to extract adatom interaction energies for such adsorbates.

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16. The repulsive interaction determined here is, of course, sensitive to the magnitude of $-\epsilon_a$, which in turn depends on the assumption $\epsilon_a = \epsilon_{2b}$. On the basis of the formation of the diffraction pattern, a physically reasonable relaxation of this assumption causes ϵ_b 's to vary less than +50%.

FIGURE CAPTIONS

Figure 1. Structure model of $p(2 \times 1)$ island on a bcc (110) substrate.

X's indicate sites occupied by O atoms, labeled the r-sublattice in the text. Filled circles indicate unoccupied sites. Within an island, these are termed the s-sublattice. ϵ_a , ϵ_b , ϵ_{2b} represent interactions between sites as indicated by the unit vectors.

Figure 2. Temperature dependence of the $(1/2 \ 1/2)$ superlattice reflection at high and low coverage and comparison to model calculation.

a) low coverage $\theta = 0.25$;

b) saturation $p(2 \times 1)$ coverage $\theta = 0.53$. Note the different transition temperatures and shapes of the curves.

Figure 3. Experimental transition temperature vs. coverage. $\theta = 0.5$ corresponds to saturation coverage for the $p(2 \times 1)$ structure.

