

Temperature dependence of the phase diagram of Cl/Ag(100)

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Using low-energy electron diffraction, we have determined the coverage at which overlayers of Cl adsorbed on Ag(100) order into a $c(2\times 2)$ structure for sample temperatures ranging from 300 to 500 K. We find no evidence for a variation in the critical coverage θ_c over this temperature range. However, experimental uncertainties in the values of θ_c are too large to rule out the small variation predicted by an interacting-hard-square model with only next-nearest-neighbor repulsions. We find that the addition of modest third-neighbor repulsions to the model improves agreement of transfer-matrix scaling calculations with experimental measurements.

INTRODUCTION

The interactions between chemisorbed surface atoms are clearly important to the understanding of many surface processes. In general, however, there is no reliable method for predicting these interactions. It is therefore desirable to determine the adatom-adatom interactions for as many systems as possible, with the hope of exposing underlying principles. Rather perversely, even though adatom-adatom interactions profoundly affect many surface processes, they are generally weak compared to adatom-substrate interactions, and are, therefore, difficult to quantify experimentally. One approach to estimating the interactions is to compare measured phase diagrams with model (lattice-gas) phase diagrams. The goal of this work is to measure the high-temperature phase boundary separating the $c(2\times 2)$ phase of Cl/Ag(100) from the disordered phase and to estimate from this the Cl-Cl interaction energies, or at least specify a model which gives a consistent phase diagram.

Cl/Ag(100) has been studied by many groups.¹⁻⁴ Chlorine molecules dissociate upon chemisorption and the only ordered structure seen is a $c(2\times 2)$ overlayer. The Cl atoms are believed to form a simple overlayer: A controversy about the geometry of the $c(2\times 2)$ structure has been recently resolved.⁴ Figure 1 shows this structure and

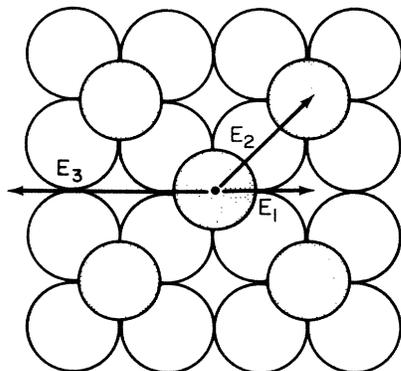


FIG. 1. A schematic picture of the $c(2\times 2)$ structure of Cl adsorbed on Ag(100) with relevant lattice-gas-model interactions. In this work, E_1 is taken as infinitely repulsive.

relevant Cl-Cl interactions within a lattice-gas model.

Assuming the Cl Auger signal to be directly proportional to Cl coverage, which should be a good approximation at submonolayer quantities, a linear increase in coverage with exposure to Cl_2 up to a well-defined saturation coverage was observed. The work function of the surface also increased linearly with Cl coverage above $\theta \cong 0.01$ monolayers (ML). The intensities of low-energy electron-diffraction features due to the $c(2\times 2)$ phase also reach a maximum at the saturation coverage. As the temperature of the saturated surface was raised, Cl began to desorb before the $c(2\times 2)$ phase disordered. These observations suggest that only one type of binding site is occupied, so that the system can be modeled by a square lattice gas, and that the saturation coverage is 0.5 ML; that is, that the nearest-neighbor interaction energy E_1 is effectively infinitely repulsive and the Cl atoms act as hard squares in blocking out neighboring sites.

A number of other chemisorbed systems on square surfaces exhibit $c(2\times 2)$ structures at 0.5 ML; the phase diagrams of several systems have been studied: Se/Ni(100) (Ref. 5); O/Ni(100) (Ref. 6); and O/Pd(100).⁷ In addition to the $c(2\times 2)$ phase at coverages near 0.5 ML, these systems have a $p(2\times 2)$ phase at coverages near 0.25 ML. This is not surprising as further neighbor interactions can naturally stabilize lower coverage phases: third-neighbor attractions⁸ or fourth-neighbor repulsions⁵ can create a $p(2\times 2)$ phase. No low-coverage phase is seen for Cl/Ag(100), however, even for temperatures as low as 90 K. As we will discuss later in this paper, the absence of other phases at low coverages places restrictions on the values of the interaction energies consistent with experiment.

The $c(2\times 2)$ phase of Cl/Ag(100) appears only after the coverage has reached a particular critical value θ_c . Taylor *et al.*¹ studied this order-disorder phase transition at 300 K. They estimated θ_c to be 0.394 ± 0.007 ML. If there were *only* first-neighbor exclusions, that is, if the system were equivalent to the much studied hard-square model, the value of θ_c would be approximately 0.368 ML (Ref. 9) and it would be independent of temperature. It was found that the experimental value of θ_c could be accounted for by assuming the presence of a second-neighbor repulsion of between 20 and 26 meV. If this model is correct, the phase boundary should exhibit some temperature dependence, with θ_c varying from 0.388 ML

at room temperature to 0.381 ML at 600 K for $E_2=24$ meV. Smaller values of E_2 would result in a weaker temperature dependence and smaller values of θ_c . In this paper we report on measurements which test this prediction. We find no statistically significant evidence for a temperature variation in the phase boundary. To try to account for our observations, we introduce a third-neighbor repulsion. We emphasize at the outset that such an intricate interpretation of the experiment neglects many effects which could plausibly be present. For example, we neglect finite-size-induced shifts in the estimated θ_c caused by the limitation of the size of the correlation length due to the finite distance between quenched defects, we ignore effects caused by the presence of impurities, and we do not consider effects of longer ranged interactions.

EXPERIMENT

Experiments were performed in a standard stainless-steel UHV bell jar equipped with hemispherical retarding field LEED (low-energy electron diffraction)/Auger optics, a quadrupole mass spectrometer, and an Ar^+ sputtering gun. The base pressures were less than 10^{-10} Torr. Cl_2 was admitted through a variable leak valve and the pressure measured with an ion gauge near the leak valve. The Cl_2 pressure at the sample was lower than measured at the ion gauge due to the pumping of the reactive Cl_2 by the chamber walls. The $\text{Ag}(100)$ sample cleaning and preparation has been reported previously.¹ The sample was mounted on a resistive heater and temperature was monitored to within 5 K by a chromel-constantan thermocouple embedded in the sample.

LEED beam intensities were measured with a spot photometer consisting of a camera lens focusing the desired beam onto a small aperture located in front of a photomultiplier tube. To avoid distortions due to the heater current, the electron beam and heater current were chopped on alternate cycles at 170 Hz during measurement. Changes in the work function were measured using the diode method¹⁰ using the electron gun in the LEED optics. A simple electronic feedback loop was used to monitor the work function change continuously during Cl_2 exposure. Shifts in work function could be measured with a resolution of 20 meV.

RESULTS

The critical coverage was determined from the intensity of the $(1/2,1/2)$ beam of the chlorine $c(2 \times 2)$ LEED pattern at 65 eV as a function of Cl_2 exposure. To convert the measured exposures to absolute coverages, we made use of the constant sticking coefficient below saturation.¹ The measurements were begun at a coverage of around 0.25 ML as measured using Auger-electron spectroscopy (AES). The sample was then exposed to Cl_2 at a pressure of approximately 2×10^{-9} Torr held constant to about 1%. The intensity was measured as a function of time and the exposure was ended at a coverage of about 0.45 ML. The final coverage was then measured precisely using AES. The coverages were interpolated from the measured

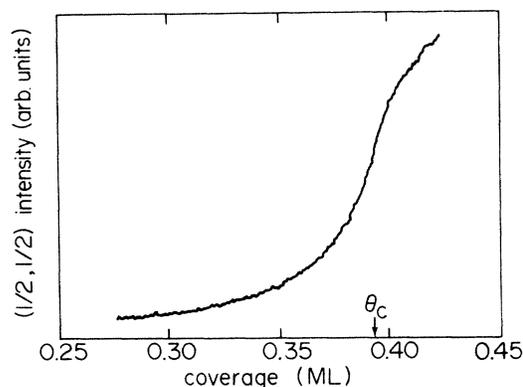


FIG. 2. Sample plot of half-order diffracted intensity vs coverage. The method of coverage calibration is described in the text. The critical coverage is estimated from the point of inflection of this curve.

initial and final values resulting in traces of intensity versus coverage as shown in Fig. 2. The precision of the coverage measurement was determined from repeated measurements of the Auger signal to be ± 0.007 ML. The critical coverage was determined from the inflection point of the variation of intensity with coverage.¹¹ The inflection point was determined by numerically calculating the first derivative of the $I-\theta$ curve. The uncertainty in determination of the inflection point was much less than the uncertainty in the coverage measurements. Similar measurements were repeated for several temperatures between 300 K and 570 K in order to construct the temperature-dependent phase boundary shown in Fig. 3.

In making the coverage calibration we assumed that the sticking coefficient remains coverage independent at higher adsorption temperatures. To confirm this we measured the work-function shift, which is linear with coverage at room temperature, as a function of exposure.¹ We

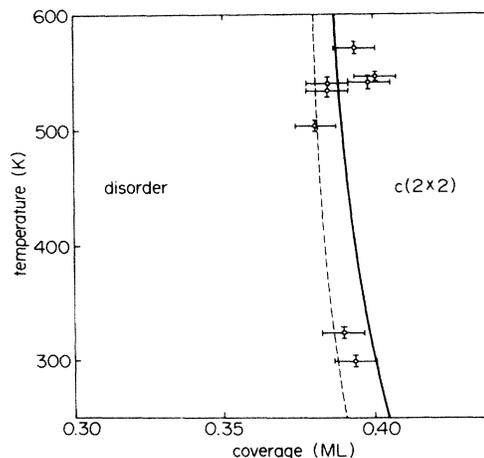


FIG. 3. Experimental phase diagram (points) compared to model hard-square lattice-gas phase diagrams: $E_2=24$ meV and $E_3=0$ (dashed line), and $E_2=23$ meV and $E_3=3.5$ meV (solid line).

do not expect the work function to be temperature dependent. At the highest temperature measured, 620 K, deviations from linearity occur only above 0.475 ML, well above the maximum coverage used for calibration.

DISCUSSION

In using the experimentally determined phase diagram to deduce values for the adatom interaction, it is crucial that the measured values of the coverage be accurate. We have estimated the precision of the coverage measurements to be ± 0.007 ML. However, it is also necessary to consider the possible effect of any systematic error on the accuracy of the measurement. We feel the most obvious source of systematic error to be adsorption of Cl into defect sites. Three cases are possible: (1) the ordered $c(2 \times 2)$ structure may fill first, followed by the defect sites; (2) the $c(2 \times 2)$ and defect sites may fill simultaneously; and (3) the defect sites may fill first, followed by the $c(2 \times 2)$ sites.

In the first case, the measured coverage would be lower than the true value in the ordered regions. However, the LEED intensity would also reach its maximum before the AES intensity, which is not observed. Therefore, we can rule out this case. In the second case, the total surface coverage would be greater than one half a monolayer, but the local coverage in the ordered regions would agree with the measured value. In the third case, the measured values would be larger than the true coverage in the ordered regions. The small nonlinearity observed in the change in work function with coverage¹ at small coverages allows us to estimate the maximum value of this effect to be ~ 0.01 ML. Therefore, if there is a systematic error in the coverage calibration, the measured values are larger than the true value by at most 0.01 ML.

Figure 3 compares two model phase diagrams with experiment. The dashed line shows the diagram for the hard square model with only second-neighbor repulsions with E_2 chosen equal to 24 meV. This value gives the best agreement with experiment: Making E_2 larger does shift the critical coverages to higher values¹² but at the expense of causing a (2×1) phase, which occurs around 1/4 of a monolayer,¹² to appear at temperatures above 90 K, which is not observed.¹ The accuracy of the transfer-matrix scaling calculation, which produced this phase diagram,¹² is probably better than the resolution of Fig. 3. This model phase diagram is not grossly inconsistent with experiment. However, if one neglects the possibility of systematic error in the absolute coverage calibration, the model does tend to underestimate θ_c .

This small discrepancy can be repaired by introducing a small repulsive E_3 . The solid line in Fig. 3 shows our estimate of the phase diagram for $E_2 = 23$ meV and $E_3 = 3.5$ meV. This phase diagram was computed in essentially the same manner as in Ref. 12; exact information from semi-infinite strips of sites was extrapolated to the infinite system limit. However, because of the larger range of the interactions smaller strip widths were used. The curve for nonzero E_3 was constructed by extrapolating results¹³ from strips 4, 6, 8, and 10 sites wide. By studying the ac-

curacy of the calculation for $E_2 = 0$ for these widths we estimate the accuracy of the critical coverages to be approximately 0.001.¹³ Unfortunately it is much more difficult to generate accurately the low coverage parts of the phase diagram when E_3 is nonzero. For even quite large positive values of E_3 ($0.25E_2$), transfer-matrix scaling yields a high-temperature part of the low coverage phase diagram which is very similar to the case $E_3 = 0$.¹² There is a narrow (2×1) phase between 0.24 and 0.26 ML. The maximum transition temperature is difficult to determine, however. For example, for the interaction set of Fig. 3, comparison of strips of width 4 and 6 give a maximum 2×1 transition temperature of 74 K, 4 and 8 give 70 K, but 6 and 8 give 63 K: There is no sign of convergence. We also searched for a low-temperature $c(4 \times 2)$ phase which should occur when E_3 is repulsive. There is no sign of this phase above $T = 20$ K. By performing Monte Carlo simulations for the two models on 24×24 lattices (being careful that averages were independent of starting configurations, which required waiting on the order of 10^4 Monte Carlo steps per site for equilibration) we established that there was also no significant *short-range* (2×1) order at 90 K, so that both the interaction sets are consistent with experimental observations at low T . Because of metastability problems, however, the Monte Carlo calculations were unable to provide equilibrium properties much below 90 K.

A natural question now is "Can one place meaningful restrictions on the values of E_3 and E_2 consistent with the experimental phase diagram?" The answer turns out to depend critically on the size of the errors in the phase diagram. Figure 4 (solid line) shows the allowed values of E_2 and E_3 if one interprets the experimental data in Figure 3

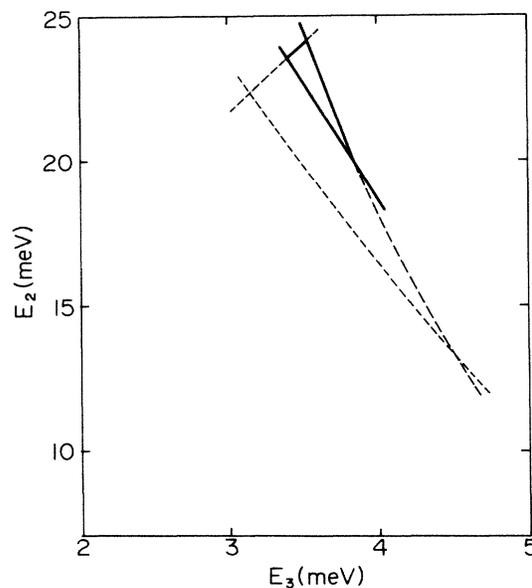


FIG. 4. Values of E_2 and E_3 which are consistent with the experimental phase diagram: Assuming the phase boundary is between 0.387 and 0.401 ML between 300 and 600 K gives the region enclosed by the solid line; and assuming it is between 0.386 and 0.401 ML gives the region determined by the dashed line.

as requiring the phase boundary to lie between 0.387 and 0.401 ML in the temperature range 300 to 600 K. The requirement that there be no low coverage phase above 90 K (Ref. 14) restricts the system to be beneath the line with positive slope. The allowed range of E_2 and E_3 is rather small: Smaller values of E_3 are ruled out because of the appearance of (2×1) order, larger values are not allowed because then the model phase diagrams fall outside of the specified coverage range. If, however, one changes the allowed coverage range by just 0.001 ML so that coverages from 0.386 to 0.401 are allowed, the range of allowed values of E_2 and E_3 increases dramatically (dashed lines in Fig. 4; note that the accuracy of the finite-size scaling calculation is not negligible here). So, even ignoring other complications, as discussed in the Introduction, not a lot can be quantitatively said about the sizes of E_2 and E_3 , given the ambiguities in interpreting the experimental uncertainty in the phase boundary. Given Fig. 4, however, it seems reasonable to say that E_2 is on the order of 10 meV and E_3 is less than 10 meV.

In contrast, if we take into account the possibility of systematic error in the coverage calibration, then the observed phase diagram can be explained without recourse to a third-neighbor interaction. The average value of θ_c measured between 300 and 600 K is 0.391 ML. If we assume this is too large by 0.01 ML due to systematic error, then the true value would be 0.381 ML. With this value of θ_c , the phase diagram could be explained with an interaction set of $E_2 \cong 15$ meV and $E_3 = 0$. This results in a temperature variation of θ_c of only 0.006 ML between

300 and 600 K, which is in better agreement with the data. It also suppresses the formation temperature of the (2×1) phase to ~ 50 K, well below the lowest temperature of observation.

CONCLUSION

We have presented the temperature dependence of the phase diagram for $c(2 \times 2)$ Cl/Ag(100), and have shown that there is no difficulty in interpreting the results in terms of an interacting-hard-square lattice-gas model. Unfortunately, the featurelessness of the phase diagram and uncertainties in the coverage calibration do not allow us to unambiguously determine the Cl-Cl interaction energies beyond the observation that values of the repulsive interaction E_2 on the order of 10 meV and values of E_3 less than 10 meV are consistent with the experimental phase diagram. To determine the interactions more accurately, or to test the model more fully, one needs an even more accurate determination of the phase boundary or observations of the predicted low- T phases.

ACKNOWLEDGMENTS

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¹³As an example of the convergence we list the results for $E_2 = 1$, $E_3 = 0.15$, and $T = 1.0$: comparing strips of width 4 and 6 gave $\theta_c = 0.40275$; 6 and 8 gave $\theta_c = 0.40233$; and 8 and 10 gave $\theta_c = 0.40210$. Extrapolating these values in the standard way by a power-law fit gives the final estimate of θ_c as 0.4014. For comparison the sequence of estimates for the case $E_2 = E_3 = 0$ for the same strip widths is 0.36939, 0.36839, and 0.36807 which extrapolates to 0.3678. This compares with the estimate of 0.367743(1) using strip widths up to 22 (see Ref. 9).

¹⁴The estimate of the maximum transition temperature of the (2×1) phase was taken from the comparison of strip widths 4 and 6: This comparison gave higher estimates of the transition temperature than those using strips of width 6 and 8, and 10 and 12, as described in the text.

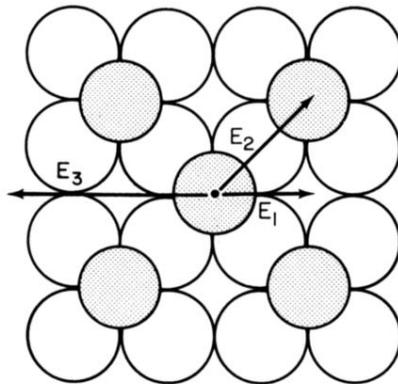


FIG. 1. A schematic picture of the $c(2 \times 2)$ structure of Cl adsorbed on Ag(100) with relevant lattice-gas-model interactions. In this work, E_1 is taken as infinitely repulsive.