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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → A summary of the experimental and theoretical results of studies of phase transitions on clean and adsorbate covered surfaces is given. A complete list of publications and talks resulting from this work is included.		

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Final Report

PHASE TRANSITIONS ON CLEAN AND ADSORBATE COVERED SURFACES

by

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1. INTRODUCTION

This Final Report summarizes the scientific results obtained during our project entitled "Phase Transitions on Clean and Adsorbate Covered Surfaces."

2. SUMMARY OF EXPERIMENTAL WORK

Cont'd → The experimental studies are divided among three categories: (1) Surface Phases of Se Adsorbed on Ni(001); (2) Au(110) (1x2) Order-Disorder Transition; (3) Experimental Methods for Study of Surface Phase Transitions. These are presented in order. Interpretation of the experimental results relied heavily upon the theoretical work described in Section 3.

2.1. Phase Diagram of Submonolayers of Se Adsorbed on a Ni(001) Surface

Cont'd DD1473 → The thermodynamic phase diagram for sub-monolayers of Se adsorbed on a Ni(001) substrate has been determined and the characteristics of the phase transitions in the vicinity of the phase boundaries have been studied. Reflection Electron Diffraction, Auger Electron Spectroscopy and Thermal Desorption Spectroscopy were the major experimental techniques employed. The major results of this study are:

1. The phase diagram has been determined for Se coverages in the range $0 \leq \theta \leq 0.5$ monolayers and for substrate temperatures between 350 K and 650 K.
2. The experimental and theoretical analysis are most consistent with all transitions being continuous.
3. Results are compared with model calculations to deduce the magnitude of the Se-Se interaction energies.
4. The Se/Ni(001) phase diagram is shown to be a possible realization of the Ashkin-Teller model.
5. Se adsorption to coverages of about one-monolayer and above leads to formation of bulk NiSe_x compounds.

A detailed presentation of the above results is made in Technical Reports #10 and #11. One Ph.D. thesis, "Thermodynamic Phase Diagram of Selenium Adsorbed on the Ni(001) Surface," by J.S. Ochab was completed. The thesis abstract is included in the Appendix.

2.2. The Au(110) (1x2) Order-Disorder Phase Transition

New Low Energy Electron Diffraction instrumentation developed as a part of this project was used to study the order-disorder phase transition which occurs on the (1x2) reconstructed surface of clean Au(110). The major results of these experiments are:

1. The Au(110)(1x2) phase transition was shown to be a realization of the simple Ising Universality Class. The critical exponents α , β , γ and ν were determined from the experimental data and agree with predicted values.
2. Evidence for finite size effects due to surface imperfections was obtained. These effects suppress the critical temperature 695 K by about 45 K and are consistent with theoretical predictions.
3. A method for extracting the critical exponent of the specific heat from a diffraction measurement proposed by Bartelt, Einstein and Roelofs was tested and shown to be valid.

These results are presented in detail in Technical Reports #12 and 14. One Ph.D. thesis, "An Investigation of the Au(110)(1x2) Order-Disorder Phase Transition," by D.E. Clark was completed as part of this study.

2.3. Experimental Methods for Study of Surface Phase Transitions

Considerable attention was given to the proper experimental and analysis methods necessary to use Low-Energy Electron Diffraction (LEED) as a tool to study phase transitions on surfaces. Major results include:

1. The limitations that non-structural parameters and multiple scattering place on the accuracy of lattice constant determination were analyzed.

2. The uncertainties introduced in extraction of critical exponents from LEED data by non-critical effects such as thermal diffuse scattering were analyzed.
3. Some artifacts introduced by multiple scattering were studied and a method to correct for them was developed.
4. A new, high coherence LEED system was developed but was found to be too mechanically unstable to take full advantage of the highly coherent primary electron beam.

These results are described in Technical Reports #3, 9, 11 and 13.

3. SUMMARY OF THEORETICAL WORK

The theoretical work falls into four categories: (1) stepped surfaces, (2) renormalization group calculations, (3) effects of finite size on phase transitions in two dimensions and (4) analysis of phase diagrams for specific experimental systems.

3.1 Theoretical Analysis of Stepped Surfaces

A theoretical analysis of some effects of stepped surfaces on ordering was carried out. The major results are twofold. A way to determine the sign of the change in binding energy at terrace edge sites directly from experimental results (Low Energy Electron Diffraction data) was developed, explored and applied to O/stepped W(110). The method used included Monte Carlo simulation. Detailed results are contained in Technical Reports #1, 2, and 4 and publications #7, 8, 9 and 17. Secondly a classification of which phase transitions on stepped surfaces are allowed to be continuous (second order) was made. This study employed the Landau-Lifshitz rules. The main results are that the symmetry breaking due to the steps reduces the number of possible continuous transitions, and most of them are on the Ising universality class. Details are given in Technical Report #5 and publication #13. This work constituted the Master's thesis of B.E. Clements. The thesis abstract is included in the Appendix.

3.2 Renormalization Group Calculations

Some calculations using the renormalization group method for first-order transitions and specific models of surface systems were carried out. Details are given in Technical Reports #5, 6, 7 and 8 and publications #10 and 14.

3.3 Finite Size Effects

Results were obtained on the shape dependence of the finite size specific heat correction term in the two-dimensional Ising model critical region. It was shown analytically that the curious unexplained effects are due to a one-dimensional array of domain walls. Details are given in Technical Report #16 and publications #15 and 16. In addition a review of the theory of finite size effects (and our results on stepped surfaces) was written, see Publication #17. Finally, using the recently developed principle of conformal invariance, calculations of scattering lineshapes in fully finite 2D regions (at bulk criticality) of various shapes were made. This represents a significant extension of the theory of finite size effects to include scattering functions. See Technical Report #17 and publications #18 and 19.

3.4 Analysis of Experimental Work

In conjunction with our experimental colleagues, analysis of results for Se/Ni(100), Au(110) and N₂/Ni(110) was made. The first two have already been described under Section 2. The last involved understanding the observed phase diagram of N₂/Ni(110), which apparently includes a phase that is formed due to an instability to dislocations. See Technical Report #18 and publication #12.

5. APPENDICES

Appendix One: List of Publications

1. "Limitations to the Accuracy of Surface Crystal Structure Determinations Using Low-Energy Electron Diffraction," W.N. Unertl and S.R. McKay, in Proceedings of a Conference on Determination of Surface Structure by Leed, Ed. P.M. Marcus and F. Jona, (Plenum Press, New York, 1985) p. 261.
2. "Phase Diagram of Selenium Adsorbed on the Ni(100) Surface: A Physical Realization of the Ashkin-Teller Model," P. Bak, P.H. Kleban, W.N. Unertl, J. Ochab, G. Akinci, N.C. Bartelt and T.L. Einstein, *Phys. Rev. Lett.* **54**, 1539 (1985).
3. "The Au(110) (1x2)-(1x1) Phase Transition: A Physical Realization of the 2D Ising Model," J.C. Campuzano, M.S. Foster, G. Jennings, R.F. Willis and W.N. Unertl, *Phys. Rev. Lett.* **54** (1985) 2684.
4. "Some Experimental Artifacts in LEED Studies of Phase Transitions," W.N. Unertl, D.E. Clark and C.S. Shern (to be published in *J. Vac. Sci. Technol.*).
5. "Specific Heat Anomaly of Au(110) (1x2) Studied by Low-Energy Electron Diffraction," D.E. Clark, W.N. Unertl and P.H. Kleban (Submitted to *Phys. Rev. B*).
6. "Continuous Phase Transitions in Two Dimensional Systems," W.N. Unertl (A review article under contract with *Comments on Solid State Physics*).
7. "Lattice Gas Models for Chemisorption on Stepped Surfaces," P.H. Kleban, *Surface Sci.*, **103**, 542 (1981).
8. "Chemisorption on Stepped Surfaces: O/Stepped W(110)," P.H. Kleban and R. Fiagg, *Surface Sci.*, **103**, 552 (1981).
9. "Chemisorption on Stepped Surfaces and Adatom Binding Energies," P.H. Kleban *Proceedings of the Conference on Ordering in Two Dimensions*, S.K. Sinha, ed., North-Holland (1980).
10. "Direct Calculation of the Derivatives of the Free Energy for Ising Models by a Modified Kadanoff's Variational Method," P.H. Kleban and Chin-Kun Hu, *J. Comp. Phys.* **43**, 289 (1981).
11. "Phase Diagram of Ising Models with Random Sublattice Vacancies," P.H. Kleban and Chin-Kun Hu, *Phys. Rev. B* **25**, 6760 (1982).
12. "Evidence for the Commensurate Solid-Fluid-Incommensurate Solid Phase Sequence: N₂ Adsorbed on Ni(110)," P.H. Kleban, M. Grunze, W. N. Unertl and F. Rys, *Phys. Rev. Letters* **51**, 582 (1983).
13. "Landau-Lifshitz Analysis for Stepped Surfaces," P.H. Kleban and B.E. Clements, *Surface Sci.* **138**, 211 (1984).
14. "Phenomenological Renormalization Group Approach to Phase Transitions," P.H. Kleban and Chin-Kun Hu, *Annual Report of the Institute of Physics, Academia Sinica* **13** (1983).
15. "Domain Walls and Shape Dependence of Finite Size Corrections to the Two Dimensional Ising Model Critical Region," P.H. Kleban and G. Akinci, *Phys. Rev. B* **28**, 1466 (1983).

16. "Domain Walls and Shape Dependence in the Two-Dimensional Ising Model Critical Region," P.H. Kleban and G. Akinci, Phys. Rev. Letters **51**, 1058 (1983).
17. "Finite Size Effects, Surface Steps, and Phase Transitions," P.H. Kleban, in Chemistry and Physics of Solid Surfaces V, R. Vanselow and R. Howe, eds. (Springer, Berlin) 1984.
18. "Finite Size Effects at Two Dimensional Ising Critical Points via Conformal Mapping," P.H. Kleban, G. Akinci, R. Hentschke, and K. R. Brownstein, J. Phys. A. **19**, 437 (1986).
19. "Effects of Finite Size and Shape on Scattering and Thermodynamic Quantities at Two Dimensional Ising Critical Points," P.H. Kleban, G. Akinci, R. Hentschke and K. R. Brownstein, Surface Science **166**, 159 (1986).

Appendix Two: List of Seminars and Talks

A. W.N. Unertl

1. "How Accurate is LEED," 26th National Symposium, American Vacuum Society, New York, October 1979.
2. "On the Accuracy of LEED Structure Determinations," W.N. Unertl, Bull. Am. Phys. Society **25** (1980) 327.
3. "Limitations to the Accuracy of Surface Crystal Structure Determinations using Low-Energy Electron Diffraction," Conf. on Determination of Surface Structure by LEED, Yorktown Heights, NY, 20 June 1980.
4. "Status of Our Ability to Determine Surface Structure," Fritz-Haber-Institute, Berlin, Germany, September, 1982.
5. "How Accurate is Low-Energy Electron Diffraction," University of Munich, Munich, W. Germany, June, 1983.
6. "Physics in Flatland: Phase Transitions on Surfaces," University of Vermont, April, 1984.
7. "Surface Phase Transitions," University of Osnabruck, W. Germany, June, 1984.
8. "Surface Phases of Se on Ni(100)," Fritz-Haber-Institute, W. Berlin, Germany, June, 1984.
9. "The Askin-Teller Model and the Ordered Phases on Se/Ni(100)," First International Conference on the Structure of Surfaces, Berkeley, August, 1984.
10. "Some Recent Experimental Studies of Surface Phase Transitions," Brookhaven National Laboratory, October, 1984.
11. "Critical Phenomena in Two Dimensions," Eastman-Kodak Corp. Research Center, Rochester, NY, October, 1985.
12. "Experimental Artifacts in LEED Studies of Phase Transitions," 32nd National Symposium, American Vacuum Society, Houston, TX, November, 1985.
13. "Phase Transitions on Surfaces: Models of Two Dimensional Systems," Colorado School of Mines, March, 1986.
14. "Critical Exponent α for the Au(110) (1x2) Order-disorder Transition," March Meeting Am. Phys. Soc., Las Vegas, April, 1986.

B. P.H. Kleban

1. "Chemisorption on Stepped Surfaces," Institute of Theoretical Physics, University of Washington, Seattle, July 1980.
2. "Diffraction Gratings, Surfaces, and Chemisorption," for the undergraduate physics club at Boston University, October 1980.
3. "Chemisorption on Stepped Surfaces," Statistical Mechanics Meeting, Rutgers University, December 1980.

4. "Specific Heat Maxima in Finite Systems," APS, Phoenix, March 1981.
5. "Criterion for First Order Phase Transitions," and "Chemisorption on Stepped Surfaces," Physics Dept., Brown University, May 1981.
6. "Criterion for First Order Phase Transitions," Statistical Mechanics Meeting, Rutgers University, May 1981.
7. "Chemisorption on Stepped Surfaces," International Conference on Phase Transitions on Surfaces, University of Maine, August 1981.
8. "Criterion for First Order Phase Transitions," NES-APS, University of Maine, October 1981.
9. "Criterion for First Order Phase Transitions," Physics Department, M.I.T., October 1981.
10. "Criterion for First Order Phase Transitions," Physics Department, University of Rhode Island, December 1981.
11. "Divergence of the Susceptibility at a First-Order Phase Transition," Statistical Mechanics Meeting, Rutgers, December 1981.
12. "Criterion for First Order Phase Transitions," APS Meeting, Dallas, March 1982.
13. "Landau-Lifshitz Analysis for Stepped Surfaces," Statistical Mechanics Meeting, Rutgers, May 1982 (this talk was co-authored and presented by B. Clements).
14. "Some Examples of Statistical Mechanics in Chemisorption Systems," Fritz-Haber-Institut, Berlin, West Germany, July 1982.
15. Poster presentation on "Criterion for First Order Phase Transitions," Conference on Statistical Mechanics of Adsorption, Trieste, Italy, July 1982.
16. Post deadline talk on " $N_2/Ni(110)$," AVS Meeting, Baltimore, Maryland, November 1982.
17. Talk on " $N_2/Ni(110)$," APS Meeting, Los Angeles, March 1983.
18. Talk on "Shape Effects in 2D Ising Models," Statistical Mechanics Meeting, May 1983.
19. Institute fur Physikalische Chemie, Universitat Munchen, July 1983 (Invited talk).
20. IUPAP Conference on Thermodynamics and Statistical Mechanics, Edinburgh, July 1983 (Contributed talk).
21. International Summer School in Surface Science, Milwaukee, August, 1983 (invited Talk); American Vacuum Society, Boston, October 1983.
22. Physics Department, Dalhousie University, Halifax, March 1984 (invited talk).
23. American Physical Society, Detroit, March 1984 (Contributed talk).
24. Physics Department, University of Maryland, April 1984 (Invited talk).

25. Statistical Mechanics Meeting, Rutgers University, December 1984 (Contributed talk).
26. American Physical Society Meeting, Baltimore, March 1985 (2 Contributed talks).
27. Physics Department, M.I.T., April 1985 (invited talk).
28. Physics Department, University of Maryland, May 1985 (invited talk).
29. International Union of Pure and Applied Chemistry Meeting, Manchester, U.K., September 1985 (Invited talk).
30. NORDITA, Copenhagen, September 1985 (Invited talk).
31. Institute for Physical Science and Technology, University of Maryland, April 1986 (Invited talk).

Appendix Three: Abstracts of Theses

$0.003 < |\epsilon| < 0.0045$.

Reconstructed Au(110) (1x2) has a surface structure described by a doubling of the periodicity in the [001] direction. As the temperature is increased, the intensity of the half-order (superlattice) diffracted beams decreases continuously and disappears leading to a (1x1) structure due to diffraction from the underlying substrate. Energy profiles of the (0, - $\frac{1}{2}$) diffracted beam were recorded for 40 eV - 80 eV (45° incident) electrons for temperatures between 477 K and 810 K. This profile has a maximum at the Bragg position (62 eV). The diffracted intensity was measured with an apertured Faraday cup detector. Corrections were made for Debye-Waller effects, the scattering factor energy dependence, thermal diffuse scattering, and instrumental effects.

The critical temperature for the transition was found to be 693 ± 6 K and is significantly larger than the previously reported value of 650 K [Campuzano et al., 1985a]. This difference is possibly due to finite size effects caused by surface imperfections in the previous work.

AN INVESTIGATION OF THE Au(110) (1x2)
ORDER-DISORDER PHASE TRANSITION

David Edward Thomas Clark

Thesis Advisor, William N. Unertl, Professor of Physics,
Department of Physics and Astronomy

An Abstract of the Thesis Presented in Partial Fulfillment of the
of the Requirements for the Degree of Doctor of Philosophy
(in Physics) May, 1986

The critical behavior of the reversible order-disorder phase transition on the clean, reconstructed Au(110) (1x2) surface was investigated using Low Energy Electron Diffraction. The universality class of this transition was shown to be in the Ising class by determining the critical exponents α and ν . The critical exponent ν describes the temperature dependence of the correlation length near the critical temperature T_c and was found to be 1.1 ± 0.1 for reduced temperatures $0.015 < t < 0.065$ where $t = (T - T_c)/T_c$. This is in good agreement with the value reported by Campuzano et al., 1985a. The heat capacity critical exponent α was determined using the method of integrated intensities [Bartelt, Einstein, and Roelofs, 1985a] and was found to be 0.0 ± 0.1 for

It is concluded that the Se/Ni(100) phase diagram may be a physical realization of a particular two-dimensional model known as the Ashkin-Teller model. The implications of this result for future studies are described.

Thermodynamic Phase Diagram of Selenium
Adsorbed on the Ni(100) Surface

By John S. Oshab

Thesis Advisor, William N. Unertl, Ph.D.

An Abstract of the Thesis Presented in Partial Fulfillment
of the Requirements for the Degree of Doctor of
Philosophy (in Physics)
May, 1985

The detailed phase diagram for submonolayers of selenium adsorbed on the Ni(100) surface has been determined for the first time using the experimental methods of Auger Electron Spectroscopy, reflection electron diffraction and thermal desorption spectroscopy. Three phases are observed: (1) an ordered $p(2 \times 2)$ phase which forms for coverages near one-quarter monolayer and temperatures below about 500K; (2) an ordered $c(2 \times 2)$ phase which forms for coverages between one-quarter and one-half monolayer; (3) a disordered phase. The characteristics of the boundaries between these phases have been examined and, although first-order transitions cannot be unambiguously ruled out, these boundaries are most consistent with continuous (second-order) transitions. The phase boundaries meet at a multicritical point near a coverage of one-quarter monolayer and a temperature of about 500K. These results are analyzed in the context of current theories of phase transitions and universality.

LANDAU-LIFSHITZ THEORY OF
SECOND ORDER PHASE TRANSITIONS
APPLIED TO STEPPED SURFACES

By Bradford Edwin Clements

An Abstract of the Thesis Presented in Partial
Fulfillment of the Requirements for the Degree of
Master of Science (in Physics).
May, 1982

This paper presents a discussion of order-disorder (continuous) phase transitions on stepped surface substrates. The Landau-Lifshitz rules are used as criteria for determining superlattice structures that can be reached by continuous phase transitions. A general method that allows one to use the two dimensional results of Rottman to determine the three dimensional stepped surface density functions describing the superlattice structures is presented. This method is applied to eleven stepped fcc and bcc surfaces which have (100), (110), and (111) terrace orientations and $p1$, $p1m1$, and $c1m1$ space group symmetry. Examples of stepped surface density functions and adsorbate superlattice structures allowed by the Landau-Lifshitz rules are given for the stepped surfaces $(bcc)[3(110) \times (0\bar{1}\bar{1})]$, $(fcc)[3(100) \times (1\bar{1}\bar{1})]$ and $(bcc)[3(110) \times (11\bar{2})]$. Finally, the results of Rottman are employed to determine that all the continuous phase transitions on the eleven stepped surfaces fall into the Ising model or the X-Y model with cubic anisotropy Universality classes.

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