ORDER–DISORDER PHASE TRANSITION OF THE Ge(0 0 1) SURFACE

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The order–disorder phase transition of the Ge(0 0 1) surface can be described by taking into account only electrostatic interactions between the asymmetric dimers. The transition fits approximately the two-dimensional Ising universality class and accordingly the critical exponent of the order parameter, β, has a value near 1/8 and is observable from an analysis of diffraction intensities. The charge transfer between the up and down atom of the asymmetric dimer consistent with the observed phase transition temperature is about $0.08e$.

INTRODUCTION

THE Ge(0 0 1) SURFACE is a prototypical example of a system possessing both a strong short-range reconstruction and a moderate range, energetically weaker one. The basic (2 × 1) reconstruction is generally accepted to entail the formation of dimers, created by pairing of nearest-neighbour surface atoms [1]. Hence, the energy involved is due to chemical bond formation. If this was the only ordering mechanism, a (2 × 1) surface unit cell would result. Larger unit cells reported (p(2 × 2) and c(4 × 2)) have usually been explained in terms of a longer-range, energetically weaker ordering of neighbouring dimers [2–7]. The Ge(0 0 1) surface has been investigated with the scanning tunneling microscope (STM) [2]. An asymmetric dimer reconstruction is observed that does not require vacancy type defects for stabilization at room temperature. Regions of local (2 × 1), c(4 × 2) and p(2 × 2) symmetry are found to coexist and the atomic positions in these regions are modeled using different arrangements of asymmetric buckled dimers. The dimers are thought to be asymmetric in the sense that the dimer bond axis is not parallel to the surface plane: one atom buckles away from the surface, while the other buckles in. Lambert et al. [3], using He diffraction, report c(4 × 2) and p(2 × 2) symmetries at temperatures below 150 K in agreement with Kevan [4], who observed a low energy electron diffraction (LEED) peak indicative of c(4 × 2) and a smaller LEED peak indicative of p(2 × 2) at temperatures below 220 K. However, this disagrees with the results of Culbertson et al. [8], who report only c(4 × 2) diffraction patterns at low temperature. In fact a transition on Ge(0 0 1) from a room-temperature nominal (2 × 1) structure to a low temperature c(4 × 2) was observed by LEED [4]. Subsequently, the transition was shown to be an order–disorder transition and was found to be accompanied by an insulator-metal transition using angle-resolves photo-emission [9]. Another interesting feature reported by Kevan [4] is that the phase transition proceeds by a two-stage process: at ~250 K the dimers in a particular row perpendicular to the dimer bond are aligned in a one-dimensional antiferromagnetic way, but the orientation of these dimer rows with respect to one another remains random until ~220 K.

Phase transitions occur because all systems in thermodynamic equilibrium seek to minimize their free energy, $F = U - TS$. One phase will supplant another at a given temperature because different states partition their free energy between U and $-TS$ in different ways. The competing phases are characterized in terms of an order parameter (e.g. in our case represented by the intensity of a low energy electron diffraction (LEED) spot, related to the ordered low temperature reconstruction which varies as $(1 - T/T_c)^{2\beta}$).

The behaviour of the order parameter near the transition temperature, T_c, distinguishes two rather different transformation scenarios. A discontinuous change in the order parameter occurs at a first-order transition. The system abruptly changes from one distinct equilibrium phase to a second distinct equilibrium phase. By contrast, two competing phases become indistinguishable at T_c for a continuous phase transition. Here, the order parameter rises smoothly from zero as the temperature is lowered, although there are large fluctuations around its mean value. One typically finds that the order parameter at a

continuous transition varies as $(1 - T/T_c)^\beta$ for T near T_c. Moreover, the numerical value of the critical exponent β (and a few other related exponents) only depends on a few physical properties, e.g. the symmetry of the system, the dimensionality of the order parameter (scaler, vector, etc.) and the dimensionality of the system. This property is called universality and suggests that interesting things can happen at a surface — the effective dimensionality is two rather than three. Scientists have long sought ideal examples of two-dimensional phase transitions to test the theories, and recently one such case has been reported. The $(2 \times 1) \rightarrow (1 \times 1)$ reconstructive phase transition that occurs for the Au(1 1 0) surface provides an elegant example of the concept of universality [10]. Experiments show that the high temperature (1×1) structure reversibly transforms to the "missing row" structure at about 650 K. The temperature dependence of the order parameter (the intensity of LEED superlattice reflections unique for the (2×1) phase) near T_c exhibit a value of the critical exponent $\beta = 0.13 \pm 0.02$ in agreement with the famous exact result of Onsager (1/8) [11].

The purpose of this paper is to report that the disorder–order phase transition of the Ge(0 0 1) surface fits approximately the $2D$ Ising universality class. The phase transition temperature will be estimated using the two different interaction constants in the two perpendicular directions and Onsager's exact solution [11].

RESULTS AND DISCUSSION

Determination of the ordered structures and phase transition leads to the issues of critical phenomena, encapsulated in the critical exponent values. The order–disorder phase transition discussed here is suggested to belong to the two-dimensional Ising universality class. Accordingly, the order-parameter exponent β has a value of 1/8, and is observable from an analysis of diffraction intensities [4]. The temperature dependence of the order–parameter (obtained from the intensity of the LEED superlattice reflection unique for the $c(4 \times 2)$ phase) for the continuous structural transition of Ge(0 0 1) is given in [4], see Fig. 1. Onsager's exact solution of the two-dimensional Ising model is also displayed (solid curve). However, as indicated by Kevan [4] himself his LEED data are not of sufficient accuracy to extract correct critical exponents and temperatures. But it is clear from Fig. 1 that the critical exponent of the order–parameter has a value near 1/8 (the intensity varies as $(1 - T/T_c)^{2\beta}$). Only the data in the temperature range from $T/T_c = 0.9$ to $T/T_c = 0.99$ ($T_c \approx$
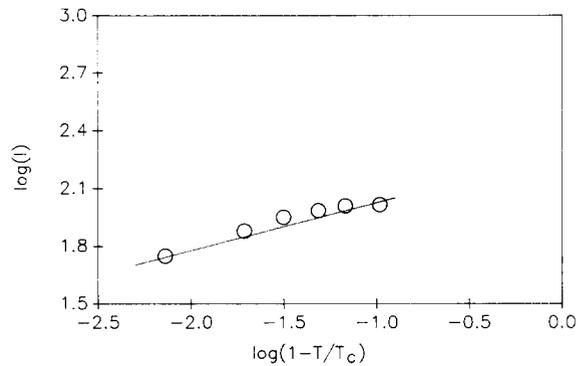

Fig. 1. Logarithm of the intensity of the $c(4 \times 2)$ spot at temperatures below $T/T_c = 0.99$ vs the logarithm of $(1 - T/T_c)$ as measured by Kevan [4] (circles). For comparison a curve with slope 1/4 is also shown (Onsager's exact solution of the two-dimensional Ising model).

234 K) are used for the power law fit as will be discussed below [14]. Because of this narrow temperature range, the Debye–Waller factor has not been divided out. The amplitude obtained from the power law fit is not universal, and therefore cannot be directly compared to the predictions of Fisher [15].

To predict the corresponding phase transition temperature one maps the dimer reconstruction to a two-dimensional Ising spin reconstruction as originally proposed by Ihm et al. [12]. We considered the effective spin Hamiltonian (see Fig. 2).

$$H = -\tfrac{1}{2} \Sigma_{x,y}\ s_{x,y}[v_1(s_{x-1,y} + s_{x+1,y})$$
$$+ v_2(s_{x,y-1} + s_{x,y+1})$$
$$+ u(s_{x-1,y-1} + s_{x-1,y+1} + s_{x+1,y-1} + s_{x+1,y+1})]$$
$$(1)$$

to describe the (2×1) family of dimer reconstructions. The terms involving interactions like $s_{x,y}s_{x,y+1}s_{x+1,y}$ $s_{x+1,y+1}$ and $s_{x,y}s_{x,y+2,y}$ contribute equally to the total energies for all four symmetries and are initially set equal to zero. To obtain the relations between the interaction constants, the mean energies $E_i = \langle H_i \rangle$ of various ordered phases at $T = 0$ K should be compared. The energies of the four members of the (2×1)
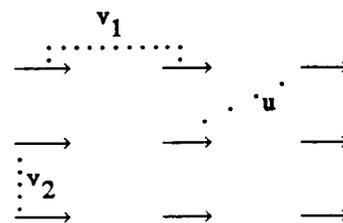

Fig. 2. Effective couplings between adjacent dimers.

Table 1. Total energies for the (2 × 1) *family of the Ge*(0 0 1) *surface* (*per spin in the Ising model or per dimer of the Ge*(0 0 1) *surface*). *The disordered nonbuckled* (2 × 1) *reconstruction is taken as zero of energy* (*data taken from* [7]). *C is a constant and has the same value for all the four different reconstructions* [7]. *The charge transfer between the up atom and the down atom of the asymmetric dimer,* Γ, *has been estimated to be smaller than* 0.1e [13]

Phase notation		Energies (per spin/dimer)	
magnetic		Ising model	dimer model [meV]
Ferromagnetic	$b(2 \times 1)$	$-v_1 - v_2 - 2u + C$	$645\Gamma^2$
Antiferromagnetic	$c(4 \times 2)$	$v_1 + v_2 - 2u + C$	$-1309\Gamma^2$
Layered antiferromagnetic (a)	$p(2 \times 2)$	$-v_1 + v_2 + 2u + C$	$-1610\Gamma^2$
Layered antiferromagnetic (b)	$p(4 \times 1)$	$v_1 - v_2 + 2u + C$	$3868\Gamma^2$

family are presented in Table 1 [7]. In [7] the asymmetric dimer of the Ge(0 0 1) surface is replaced by a dipole, $\mathbf{p} = \Gamma e \mathbf{L}$, where Γ is the charge transfer between the up and down atom of the asymmetric dimer and $\mathbf{L}$ is the distance between both atoms. The energies of the four different members of the (2 × 1) family are calculated by taking only electrostatic interactions between the dimers into account [7]. As can be shown easily [7], for the two-dimensional case dipole–dipole interactions converge rapidly. The charge transfer has been estimated to be lower than 0.1e [13] and $\mathbf{L}$ is approximately the Ge–Ge bulk bond length (2.45 Å). Further details of the energy calculations are found in [7]. The $T = 0$ K values of v_1, v_2 and u can be derived from the energy differences of the four members of the (2 × 1) family ($v_1 = 882\Gamma^2$ meV, $v_2 = -1857\Gamma^2$ meV and $u = 366\Gamma^2$ meV) as shown in [7]. As can be seen by the relative magnitude of v_1, v_2 and u, the strongest coupling between dimers is along rows. If we include only nearest neighbour interactions (v_1, v_2) and neglect the diagonal interaction, u, the exact solution of Onsager [11] can be used

$$1 = \sinh (2|v_1|/kT_c) \sinh (2|v_2|/kT_c) \tag{2}$$

resulting in a phase transition temperature of 234 K for a charge transfer of 0.082e between the up and down atom of the asymmetric dimer [13]. A possibility to account for some of the rounding in Fig. 6 in [4] of the transition at the highest temperatures would be a finite-size effect. If we suppose that this effect is the same as for the 2D Ising systems, we would compare Kevan's results to simulations of finite 2D systems by Landau [14]. For Landau's $N = 60$ result, the tail in the simulation at high temperatures is larger than that observed in Kevan's data [4], yet the shape of the curve is not appreciably affected at temperatures where the normalised intensity is greater than 0.5. We conclude that the determination of β which is about 1/8 in the lower

temperature range would not be affected by the possible presence of finite-size domains.

We have shown that the data display critical behaviour for reduced temperatures (T_c/T) between approximately 0.90 and 0.99 with a critical exponent near 1/8, but we cannot rule out the possibility that the transition has a slightly different character in particular for temperatures closer to T_c. Although the concept of universality is determined by more critical exponents (e.g. correlation length) the similarities between the Ge(0 0 1) phase transition and the finite-size 2D Ising system [14] are revealing.

CONCLUSIONS

We conclude that the Ge(0 0 1) order–disorder phase transition fits approximately the two-dimensional Ising universality class. The calculated phase transition temperature is in good agreement with experiments (220–260 K) using a charge transfer between the up and down atom of the asymmetric dimer of about 0.08e.

REFERENCES

1. R.E. Schlier & H.E. Farnsworth, *J. Chem. Phys.* **40**, 917 (1959).
2. J.A. Kubby, J.E. Griffith, R.S. Becker & J.S. Vickers, *Phys. Rev.* **B36**, 6079 (1987).
3. W.R. Lambert, P.L. Trevor, M.J. Cardillo, A. Sakai & D.R. Hamann, *Phys. Rev.* **B35**, 8055 (1987).
4. S.D. Kevan, *Phys. Rev.* **B32**, 2344 (1985).
5. M. Needels, M.C. Payne & J.D. Joannopoulos, *Phys. Rev. Lett.* **58**, 1765 (1987).
6. M. Needels, M.C. Payne & J.D. Joannopoulos, *Phys. Rev.* **B38**, 5543 (1988).
7. H.J.W. Zandvliet, G.P.M. Poppe, C.M.J. Wijers & A. van Silfhout, *Solid State Commun.* **71**, 63 (1989); H.J.W. Zandvliet, D. Terpstra & A. van

Silfhout, *J. Phys.: Condensed Matter.* **3**, 409 (1991).

8. R.J. Culbertson, Y. Kuk & L.C. Feldman, *Surf. Sci.* **167**, 127 (1986).

9. S.D. Kevan & N.G. Stoffel, *Phys. Rev. Lett.* **53**, 702 (1984).

10. J.C. Campuzano, M.S. Foster, G. Jennings, R.F. Willis & W. Unertl, *Phys. Rev. Lett.* **54**, 2684 (1985).

11. L. Onsager, *Phys. Rev.* **65**, 117 (1944), see also

B.M. McCoy & T.T. Wu, *The Two-Dimensional Ising Model,* p. 90, Harvard University Press, Cambridge Massachusetts (1973).

12. J. Ihm, D.H. Lee, J.D. Joannopoulos & J.J. Xiong, *Phys. Rev. Lett.* **51**, 1872 (1983).

13. D.H. Rich, T. Miller & T.-C. Chiang, *Phys. Rev. Lett.* **60**, 357 (1988).

14. D.P. Landau, *Phys. Rev.* **B13**, 2997 (1976).

15. M.E. Fisher, *Rep. Prog. Phys.* **30**, 615 (1967).