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A model for the W(001) surface reconstruction phase transition is studied to elucidate the dependence of transition temperature on interaction range and other model parameters. We find that for the parameter set chosen extending the range of the interaction without changing the total reconstruction energy increases the model transition temperature somewhat. This reduces a previously reported discrepancy between the experimental transition temperature and that consistent with the calculated reconstruction energy, but only marginally.

I. INTRODUCTION

The surface reconstruction transition of the W(001) surface has received steady attention since its characterization (see reviews).[1–3] After some false starts, much progress has been made on identifying and characterizing the driving force of the transition, although the picture is not yet complete. What is known is that the driving force for the reconstruction is short in range due to the involvement of states throughout the *d*-band.[4–6] The details are less clear. For example (see the discussion in Ref. 1), experiment[7] and theory seem to differ with respect to the symmetry of the surface state most directly involved in the transition. It is also unclear whether interactions between surface layer atoms dominate the effect or whether subsurface layers also play an important role in the binding. Moreover, our previous studies of models for this reconstruction transition,[8–10] have shown that the experimental value of T_c the transition temperature is difficult to rationalize with calculations of the total reconstruction energy. In this paper we report some further studies based on the models specified in Refs. 8–10, to check whether this difficulty extends throughout the conceivable parameter space, and to check whether an increase in the range of the interaction can reduce the discrepancy between experiment and state-of-the-art calculations. In Sec. II we briefly recapitulate the model. In Sec. III we present transition temperatures for two new choices for the model parameters, and in Sec. IV we present a study of the effect of increasing the range of the interaction.

II. MODEL AND PARAMETERS

Our short-range microscopic interaction model[3] is based on the microscopic displacements $\mathbf{u}_i$ of the surface-layer W atoms in the surface plane. (Displacements normal to the surface undoubtedly occur as well, but probably are not involved in the transition.[2]

$$H=\sum_{\langle ij\rangle_1}\mathbf{u}_i\Phi_1\mathbf{u}_j+\sum_{\langle ij\rangle_2}\mathbf{u}_i\Phi_2\mathbf{u}_j+\sum_i V(\mathbf{u}_i), \tag{1}$$

where $\langle ij\rangle_k$ denotes a k th neighbor pair of sites i and j and Φ_k is a 2×2 dynamical matrix expressing the interaction between a k th neighbor pair of surface atoms. $V(\mathbf{u})$ is a local (single-site) contribution to the total energy that can be viewed as arising from interaction with underlying layers of (assumed static) W atoms. We include in V only those terms allowed by the symmetry of the system, and assuming small displacements we include terms only up to fourth order in u:

$$V(\mathbf{u})=\tfrac{1}{2}Au^2+\tfrac{1}{4}Bu^4+\tfrac{1}{2}V_4u^4\cos(4\theta_i). \tag{2}$$

In Eq. (2) the terms A and B define the local potential variation with the magnitude of $\mathbf{u}$, while the term in V_4 gives the variation with θ_i, the angle made by $\mathbf{u}$ relative to the x axis.

The dynamical matrices in Eq. (1) can be written[8]:

$$\Phi_1(\mathbf{a}_1)=\begin{pmatrix}J_1+K_1 & 0\\ 0 & J_1-K_1\end{pmatrix};$$
$$\Phi_1(\mathbf{a}_2)=\begin{pmatrix}J_1-K_1 & 0\\ 0 & J_1+K_1\end{pmatrix}; \tag{3}$$
$$\Phi_2(\mathbf{a}_1+\mathbf{a}_2)=\begin{pmatrix}J_2 & K_2\\ K_2 & J_2\end{pmatrix};$$
$$\Phi_2(\mathbf{a}_1-\mathbf{a}_2)=\begin{pmatrix}J_2 & -K_2\\ -K_2 & J_2\end{pmatrix}; \tag{4}$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ denote unit vectors for the surface lattice in the x and y direction, respectively. The vector arguments of the dynamical matrices specify a bond orientation. We have previously argued that the K_1 and K_2 contributions to the potential have little effect on the character and temperature of the transition[9] and so in what follows the K's will be set to zero.

In the form of Eqs. (2)–(4) the potential is described by five parameters, A, B, V_4, J_1 and J_2. To cause the experimentally observed reconstruction pattern to occur one must choose $(J_1-J_2)>0$ and $V_4<0$. A and B must be such that the observed reconstruction actually lowers the energy, and $(B-2|V_4|)$ must be positive so that the displacements remain bounded. One can make contact with calculated potentials[4–6] by considering the energy per surface atom $E(u)$ for uniform magnitude displacement u in the $c(2\times2)$ pattern exhibited by the actual surface:

$$E(u)=-2(J_1-J_2)+\tfrac{1}{2}Au^2+\tfrac{1}{4}(B-2|V_4|)u^4. \tag{5}$$

The minimum in this energy curve,

$$E_0=-(J_1-J_2)u_0^2(1-r)=-\tfrac{1}{4}Bu_0^4(1-s), \tag{6}$$

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occurs at displacement magnitude

$$u_0 = \{[4(J_1 - J_2) - A]/(B - 2|V_4|)\}^{1/2}, \quad (7)$$

where

$$r = A/4(J_1 - J_2) \quad (8)$$

and

$$s = 2|V_4|/B. \quad (9)$$

E_0 sets the temperature scale for the simulation study of the model specified by Eqs. (1)–(3). By taking advantage of this scaling factor and by also scaling out the displacement magnitude u_0, we can reduce the parameter space that needs to be explored to just r and s as defined above and one more parameter z, which describes the contribution to driving force coming from J_2:

$$z = -J_2/(J_1 - J_2). \quad (10)$$

In Sec. IV we study the dependence of T_c on z when E_0 is held fixed to assess the sensitivity to the interaction range.

III. SIMULATION RESULTS

Our simulation code has been previously described.[8] For the new results given here we averaged in each case two independent runs of length 10 000 Monte Carlo steps (change attempts per site), at each temperature discarding the first 2000 to allow for equilibration. We determined the transition temperature from the inflection point[11] of a plot of the simulated half-order (kinematic) diffracted intensity. We found that finite-size effects were no problem at the level of accuracy sought in this survey for 12×12 lattices (periodic boundary conditions), except when $|s|$ is small. A more extensive study of finite size effects for small $|s|$ is underway.

Table I summarizes the results for the four parameter choice sets we have studied thus far. In all cases z was taken to be 0. Sets I–III do not have a small value of $|s|$. For these a lattice size of 12×12 gave adequate accuracy. A conservative error estimate for our calculated T_c's and hence also for the scaled values of E_0 (see below) is $\pm 5\%$. Set I was studied for 12×12, 24×24, and 48×48 lattices[8] to verify size insensitivity at this level. Set IV, on the other hand, was chosen to have a rather small value of $|s|$. Our results for set IV are based on the simulation of a 24×24 lattice with 30 000 Monte Carlo steps at each site.

For each set in Table I we give also a scaled value of E_0. This is the maximum reconstruction energy per site obtained by scaling the simulated transition temperature to the experimental value of 210 K.[12] This number is useful for comparing with first principles calculations of the reconstruction energy. The calculation of Terakura *et al.*[4] and Legrand *et al.*[6] were based on a semiempirical d-band approach and yielded reconstruction energies of 26 and 20 meV, respectively. That of Fu *et al.*[5] is a somewhat more sophisticated full linearized augmented plane wave (FLAPW) slab calculation, but it yields a reconstruction energy of only 10 meV. All these numbers, particularly the last mentioned, are significantly smaller than what would be needed according to our study to stabilize order up to the experimentally observed transition temperature. It is not known at present whether the calculations are not finding the full reconstruction energy or whether our incomplete survey of the parameter space has failed to include a model sufficiently close to the actual Hamiltonian. This discrepancy is large enough to render it unlikely that parameters can be found to force agreement with the result of Fu *et al.* We should note (as pointed out in Ref. 10) that the study of Legrand *et al.* indicates that a substantial energy lowering is achieved when second-layer atoms are allowed to relax. The study of Fu *et al.* fixed the positions of all but the first-layer atoms. Our study also is limited in certain ways. In the following section we explore the effect of removing one of the limitations.

IV. EFFECT OF EXTENSION OF INTERACTION RANGE

In this section we consider the effect of allowing z to become nonzero. This shifts some of the driving force of the interaction from the first to the second neighbor interactions. We adjust the strength of J_1 and J_2 complementarily so that E_0 (sim.) and u_0 are not affected, i.e., $\Delta J_2 = -\Delta J_1$. We expect that since a longer range interaction should be more effective in supporting order, T_c will be enhanced by a change of J_2 in the direction favoring $c(2\times2)$ order, i.e., negative. An increase of the simulated T_c with no change in E_0 (sim.) reduces the discrepancy discussed above. We have accordingly investigated the effects on T_c of changes in this direction.

The results of our study of parameter set III for three different values of z is shown in Fig. 1. We find that increasing z from 0 to 0.25 increases T_c by about 7% and to 0.5 by about 8%. The change is evidently saturating and even the latter, which amounts to shifting one-half of the weight of the driving force to the second-neighbor bond, only reduces the scaled value of E_0 to about -34 meV. Thus the discrepancy particularly with Ref. 5 remains large. It seems unlikely that further increases in range would be sufficient to significantly lessen the disagreement.

TABLE I. Four choices for model parameters and the implied reconstruction energies.

Set	J_1	A	B	V_4	r	s	u_0	E_0 sim.	E_0 scaled (meV)
I	1.0	−8.0	8.0	−2.0	−2.0	0.5	3	−9.0	−70
II	1.0	1.0	5.0	−2.0	0.25	0.8	3	−2.25	−35
III	1.0	0.0	3.33	−1.0	0.0	0.6	3	−3.0	−38
IV	1.0	0.0	1.53	−0.1	0.0	0.13	3	−3.0	−30

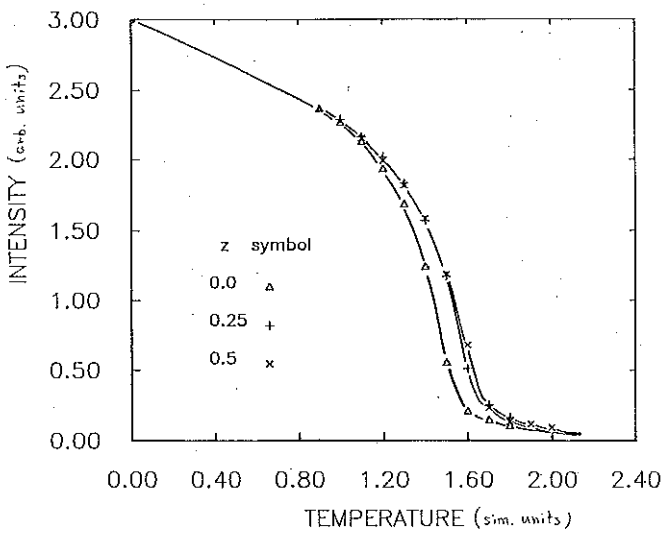

FIG. 1. Plot of simulated kinematic diffracted intensity vs temperature for interaction set III for three different values of z. The inflection point of such a plot locates the phase transition in these (12×12) lattices.

V. CONCLUSION

We have extended our survey of the parameter space of a model for the W(001) surface reconstruction. We have failed, however, to significantly lessen the discrepancy first discussed in Ref. 10 between the reconstruction energy per site implied by our study and direct, total energy, electronic structure calculations of this quantity.

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[1] J. E. Inglesfield, Prog. Surf. Sci. **20**, 105 (1985).
[2] D. A. King, Phys. Scr. **4**, 34 (1983).
[3] S. C. Ying and L. D. Roelofs, Surf. Sci. **125**, 218 (1983).
[4] I. Terakura, K. Terakura, and N. Hamada, Surf. Sci. **111**, 479 (1981).
[5] C. L. Fu, A. J. Freeman, E. Wimmer, and M. Weinert, Phys. Rev. Lett. **54**, 2261 (1985).
[6] B. Legrand, G. Treglia, M. C. Desjonqueres, and D. Spanjaard, J. Phys. C **19**, 4463 (1986).
[7] M. I. Holmes and T. Gustafsson, Phys. Rev. Lett. **47**, 443 (1981).
[8] L. D. Roelofs and J. F. Wendelken, Phys. Rev. B **34**, 3319 (1986).
[9] L. D. Roelofs, Phys. Rev. B **34**, 3337 (1986).
[10] L. D. Roelofs, Surf. Sci. **178**, 396 (1986).
[11] N. C. Bartelt, T. L. Einstein, and L. D. Roelofs, Phys. Rev. B **32**, 2993 (1985).
[12] J. F. Wendelken and G.-C. Wang, Phys. Rev. B **32**, 708 (1985).