

Diffusion and interconversion of 'defect' ad-dimers on the Si(001) 2*1 surface: a molecular statics study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 551

(<http://iopscience.iop.org/0953-8984/5/5/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 01:05

Please note that [terms and conditions apply](#).

Diffusion and interconversion of 'defect' ad-dimers on the Si(001) 2×1 surface: a molecular statics study

C P Toh and C K Ong

Department of Physics, National University of Singapore, 10 Kent Ridge Crescent, Singapore 0511, Singapore

Received 8 July 1992, in final form 26 October 1992

Abstract. We use a modified form of the Stillinger–Weber potential to obtain the binding energy and geometry of a number of Si ad-dimer structures on the fully relaxed Si(001) 2×1 surface by canonical Monte Carlo simulation. At low temperatures, we show the possible existence of two kinds of 'defect' ad-dimers which may hinder normal 1×2 growth. The mechanisms for both diffusion and interconversion of such dimers are then elucidated by examining their associated minimum-energy paths.

1. Introduction

The dynamics of Si adatoms on the Si(001) 2×1 surface has been a subject of interest in surface science for the past few years. It is expected that the fourfold symmetry breaking at the (001) surface due to the 2×1 reconstruction will result in an anisotropy in surface migration along the [110] and $[1\bar{1}0]$ directions [1]. However, symmetry breaking considerations alone will not reveal how substantial the anisotropy of the surface diffusion is. Recently, several theoretical groups have shown that surface migration is faster along the substrate dimer rows than perpendicular to them. The methods used include the first-principle total-energy calculation [2, 3] as well as molecular dynamics (MD) and Monte Carlo (MC) simulations based on classical interatomic potentials [4–7]. STM experiments have since been performed which have verified this important result [8, 9].

Recently, Dijkkamp *et al* [10] have observed the nucleation of Si clusters and their subsequent motion along the dimer rows of the Si(100) surface at temperatures around 350 K. Similar observations have been made by Lagally *et al* [11] although in both cases, the exact number of Si atoms in a cluster could unfortunately not be determined.

Despite the lack of experimental data, we suspect that such clusters are probably 'defect' ad-dimers formed during deposition at low temperatures, based on results previously obtained regarding the motion of single adatoms [4]. There, we have shown that adatoms prefer to move along the path D–A–D with occasional side trips to the trap site F (refer to figure 1). An adatom at an F site can then interact with another adatom at an adjacent F site to form an F dimer. Similarly, B dimers are formed by adatoms at the B sites. We also obtained an activation energy of ~ 0.34 eV for the diffusion. However, at low temperatures, an atom at a D site may remain there long enough until another atom appears at an adjacent D site. These two atoms

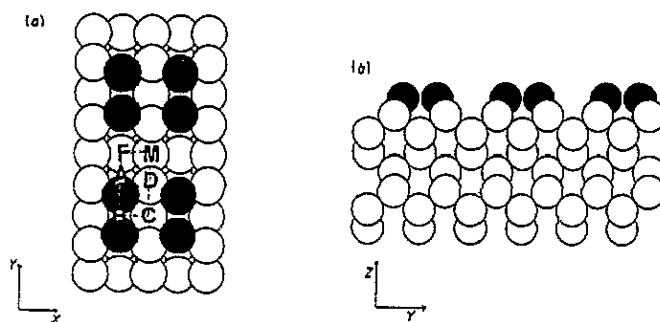


Figure 1. (a) The sites labelled by F, A, B and D are the absorption sites for a Si atom on the Si(001) 2×1 surface. M and C correspond to local maxima. Filled circles show atoms in the first layer. (b) View of Si sample in the y - z plane. Filled circles representing the dimers are clearly seen.

can then interact to form a dimer, as shown in figure 2(a) and 2(c). We call such structures 'defect' ad-dimers since they are a hindrance to the growth of regular 1×2 islands. Herein, we will label the dimer configuration shown in figure 2(a) as a D dimer and that in figure 2(c) as a D' dimer.

In this paper, we report on a study of the mobility of these 'defect' ad-dimers, notably their activation energies for the one-dimensional diffusion on top of a substrate dimer row and along the interdimer channel. We chose a modified form of the Stillinger-Weber (sw) potential as proposed by van der Eerden *et al* [12]. The original sw potential [13] describes well the stability of the diamond structure, the density increase upon melting, the cohesive energy, the lattice constant, the bulk modulus, and the bulk melting point. It also predicts correctly some of the properties of the (001) surface. However, the values obtained for the elasticity tensor do not agree well with values in the literature. We believe that the modified sw potential is more suitable for surface simulations as it has been fitted to reproduce well the elastic constants C_{11} , C_{12} and C_{44} . With this potential, we also attempt to calculate the activation energy for interconversion from one dimer configuration to another, namely D dimer \rightarrow B dimer and D' dimer \rightarrow F dimer. In the following sections, we give a brief description of the modified sw potential and simulation methods used in the present calculation. From the results obtained, we attempt to propose simple mechanisms for the diffusion and interconversion process and relate these to experimental observations.

2. The modified sw potential

The potential uses two-body and three-body terms to describe the behaviour of Si. The total energy E , in the absence of an external field, is expressed as follows:

$$E = \sum_{\substack{i,j \\ i < j}} v_2(i, j) + \sum_{\substack{i,j,k \\ i < j < k}} v_3(i, j, k) \quad (1)$$

with the i , j and k indices corresponding to different atoms. Here $v_2(i, j)$ is the two-body potential for an atom at position r_i and an atom at position r_j . It is an

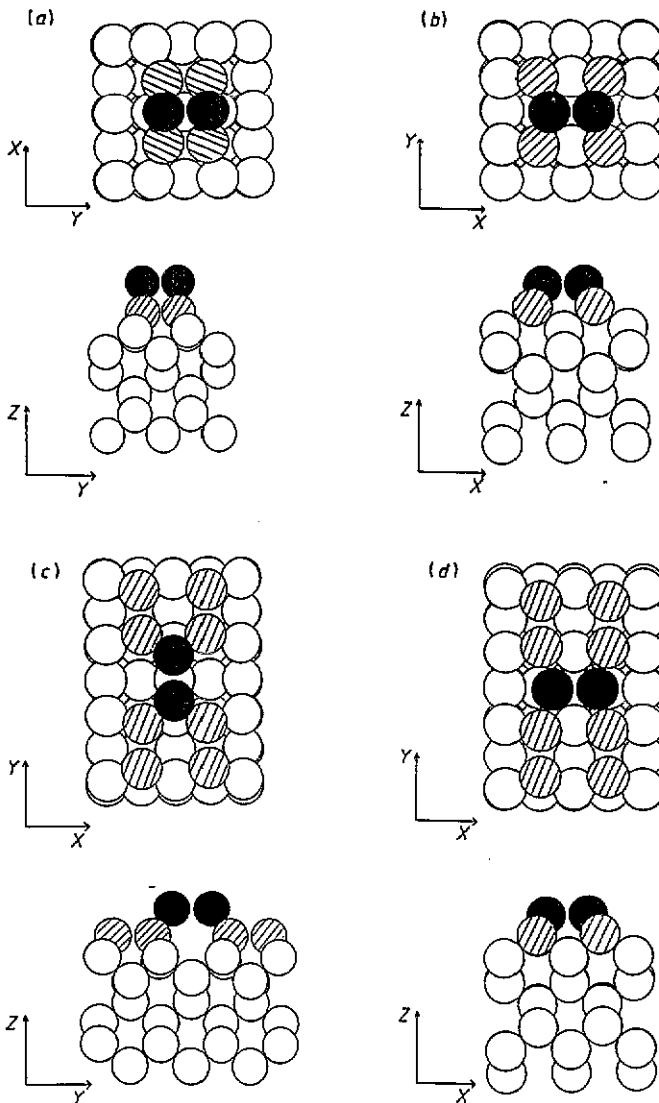


Figure 2. Schematic picture of a number of relaxed Si ad-dimer structures on the Si(001) 2x1 surface. The shaded circles denote the topmost layer atoms of the substrate, with the dimer row running in the x direction. The filled circles represent the atoms of the ad-dimer. Structures (b) and (d) are the regular B and F dimers respectively. (a) is the 'defect' ad-dimer above the substrate row (D dimer) while (c) is the 'defect' ad-dimer in the interdimer channel (D' dimer).

exponentially truncated Mie potential whose form is the same as the two-body part of the original SW potential although it has a larger cutoff at $r = a = 3.84 \text{ \AA}$ ($a \sim 3 \text{ \AA}$ for the original SW potential):

$$v_2(i, j) = \epsilon \left[\left(\sigma / r_{ij} \right)^4 - 1 \right] A(r_{ij}) \quad (2)$$

where $r_{ij} \equiv |r_i - r_j|$ and the exponential cut-off function $A(r_{ij})$ is given by

$$A(r_{ij}) = \begin{cases} \exp[b/(r_{ij} - a)] & \text{for } r_{ij} < a \\ 0 & \text{for } r_{ij} \geq a. \end{cases} \quad (3)$$

The three-body part of the potential contains three terms:

$$v_3(i, j, k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \quad (4)$$

where θ_{jik} satisfies

$$2r_{ij}r_{ik} \cos \theta_{jik} = r_{ik}^2 + r_{ij}^2 - r_{jk}^2 \quad (5)$$

and h is expressed as

$$h(r_{ij}, r_{ik}, \theta_{jik}) = CA(r_{ij})A(r_{ik})\left(\cos \theta_{jik} + \frac{1}{3}\right)^2 + k(r_{ij}, r_{ik}) = g(r_{ij}, r_{ik}, \theta_{jik}) + k(r_{ij}, r_{ik}) \quad (6)$$

Where $k(r_{ij}, r_{ik})$ is the correction factor which is a sum of two terms, each being a product of the two-body potential with a cut-off function

$$k(r_{ij}, r_{ik}) = \mu[A'(r_{ij})v_2(i, k) + A'(r_{ik})v_2(i, j)]. \quad (7)$$

The cut-off function A' is defined as

$$A'(r_{ij}) = \begin{cases} \exp[c/(r_{ij} - a)] & \text{for } r_{ij} < a \\ 0 & \text{for } r_{ij} \geq a. \end{cases} \quad (8)$$

This correction term which is absent in the original SW potential actually describes the physical effect that the strength of the bond between a pair of atoms is changed due to the presence of a third atom in the neighbourhood of the pair. For the crystal structure to be stable against collapse, the prefactor μ must be positive. Thus this factor always increases the effective bond strength with the coordination number.

The parameter set, according to van der Eerden *et al* [12], is as follows:

$$\begin{array}{llll} \epsilon = 11.2862 \text{ eV} & c = 1.06119 \text{ nm} & \sigma = 0.193767 \text{ nm} & C = 16.9907 \text{ eV} \\ b = 0.167536 \text{ nm} & \mu = 35.4811 & a = 0.384031 \text{ nm} & \end{array}$$

3. Methodology

We first obtained energies of the various ad-dimer configurations, their length and their height above the Si(001) 2×1 substrate by Monte Carlo simulated annealing. These values are given in table 1 together with those of the regular F and B dimers, which are formed by two adjacent atoms originally located at the F and B sites respectively. The sample consists of a stack of 10 layers of 14×6 atoms, each with a vacuum spacing of $\sim 8 \text{ \AA}$ above the surface. In the lateral and perpendicular directions, we had periodic boundary conditions. The atoms of each of the four dimer structures shown in figure 2 are placed about 1 \AA above the slab and the entire system is allowed to relax to its minimum energy configuration. This is achieved by first equilibrating the system at 300 K and then decreasing the temperature by 5 K for every 10 Monte Carlo steps until near absolute zero. After cooling, the system is again equilibrated until a minimum energy is attained. We have performed the above simulation using a smaller 'cooling rate' (5 K for every 100 Monte Carlo steps) and

Table 1. Energies and geometries of the structures of Si ad-dimers on the Si(001) 2×1 surface as given in figure 2. The energy values are relative to the fully relaxed clean Si(001) 2×1 surface.

Structure	Energy (eV)	Ad-dimer bond length (Å)	Height (Å) ^a
(a) D dimer	-6.27	2.48	2.00
(b) B dimer	-7.19	2.50	1.39
(c) D' dimer	-6.51	2.54	1.78
(d) F dimer	-7.95	2.53	1.19

^a Minimum *z*-coordinate difference between an ad-dimer atom and substrate atom.

conclude that the results reported here are converged to within 0.1 eV. All resultant energy values are relative to the fully relaxed clean Si(001) 2×1 surface.

We found that as in the case of the single Si adatoms, positions of the ad-dimer in the interdimer channels are more favourable than positions on the dimer rows. The two most stable structures are the F and B dimers, which come as no surprise since they correspond better with the requirements for epitaxial growth.

We consider next the thermal motion of the 'defect' ad-dimers, both along the interdimer channels and directly above the dimer rows. We propose a scheme to locate the lowest-energy path for the one-dimensional diffusion of an ad-dimer rather than constructing an energy surface for two adatoms since this will require a detailed and time consuming sampling of a four-dimensional configuration space (the (*x*, *y*) coordinates of each adatom). This is done by first displacing the centre of mass of the dimer along a straight reference line parallel to and located in the middle of the interdimer channel or above the substrate row, depending on which path the ad-dimer is taking. At each position along the line, all atoms are allowed to relax except for the two atoms in the dimer whose *x* coordinates are held fixed. This allows the ad-dimer to 'expand' or 'contract' and even 'buckle'. The dimer is then rotated so that it makes an angle ψ with the reference line. The atoms are subsequently relaxed with the following constraints on the random change in the *x* and *y* coordinates of the atoms belonging to the dimer:

$$\Delta x \tan \psi = \Delta y \quad (9)$$

$$0 < |\Delta x| \leq [6.25/(1 + \tan^2 \psi)]^{1/2}. \quad (10)$$

These will ensure that the length of the dimer can change in the direction specified by the angle ψ (note that the centre of mass of the dimer need not remain on the reference line). The second constraint prevents the dimer atoms from moving too near to or too far from one another. This process is then repeated for various values of ψ so that a minimum energy path is mapped out from one local minimum to another (refer to figure 3).

4. Results and discussions

Using the above scheme, we obtain an effective activation energy of ~0.4 eV for diffusion in the interdimer channels and ~0.57 eV for diffusion above the substrate dimer rows. These values are comparable, though higher than the activation energy for adatom diffusion computed with the same potential. Moreover, an analysis of the minimum energy path shows that the ad-dimer prefer to move with its centre

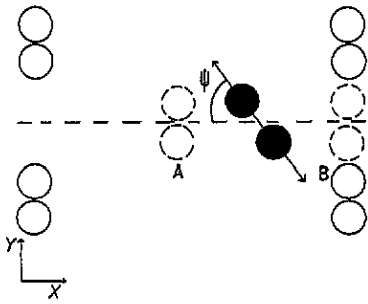


Figure 3. Schematic diagram of the scheme used to map out the minimum energy path for ad-dimer diffusion along the interdimer channel. Positions A and B represent the two local minima. The activation energy from A to B is ~ 0.33 eV and from B to A ~ 0.46 eV, giving an effective activation energy of ~ 0.4 eV. Note that the angle ψ is taken with respect to the dotted reference line.

of mass along the reference line without substantial fluctuations in the dimer length ($< 2\%$). At the same time, rotation ($\psi \neq 90^\circ$) is energetically unfavourable. In other words, 'staggered' motion of ad-dimers as found on some metal surfaces [14] is apparently absent. No significant 'buckling' of the ad-dimer is observed, which is expected, since without rotation, the atoms of the dimer 'see' approximately the same atomic environment. This means that the ad-dimer prefers to hop from one local minimum to the next by first breaking the two bonds with substrate atoms located on adjacent dimer rows or within the same row, much like a rigid dumbbell (see figure 4).

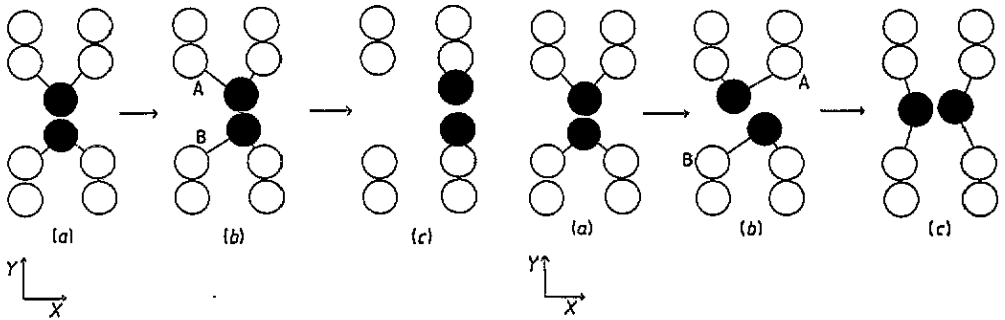


Figure 4. Schematic diagram of the diffusion process along the interdimer channel. The ad-dimer at (a) moves by first 'stretching' its bonds to atoms A and B to form the saddle point configuration at (b). (c) is finally reached by breaking these two bonds.

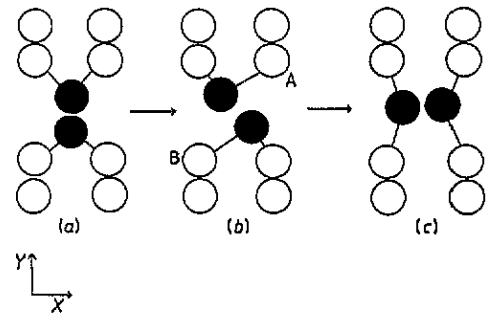


Figure 5. Schematic diagram for the interconversion process to a F dimer. The ad-dimer at (a) rotates by first 'stretching' its bonds to the atoms at A and B to form the saddle point configuration at (b). (c) is finally reached by breaking the old bond to A and forming a new bond with B and also by breaking the old bond to B and forming a new bond with A.

The two kinds of 'defect' ad-dimers can also undergo interconversion to the more stable F or B dimers. To find the most favourable path, the same scheme as above was adopted minus the translational motion. The activation energy for interconversion to a F dimer is found to be ~ 1.09 eV while the corresponding value for interconversion to a B dimer is ~ 1.02 eV. These stable dimers can also interconvert back to the 'defect' dimer configurations although the activation energies are rather high. Table 2(a) and 2(b) give the total potential energy for various values of ψ during interconversion to an F and a B dimer respectively, from which the activation energies are extracted. These values compare well with the *ab initio*

result of ~ 0.9 eV obtained by Brocks *et al* [15] for the interconversion from a D dimer to a B dimer. Again, an analysis of the minimum-energy path from one local minimum to another lead us to conclude that the dimer probably interconverts by rotating from one local minimum to another with its centre of mass more or less fixed, accompanied by minor fluctuations in the dimer length ($< 2\%$), as shown in figure 5. No significant 'buckling' is observed even though there is rotation since the centre of mass of the ad-dimer is symmetrically located. However, one must be cautious when discussing 'buckling' of ad-dimers in the context of classical simulation because classical potentials do not take into account the phenomenon of charge transfer between atoms. A displacement of the 'defect' ad-dimers, perpendicular to the substrate dimer row, by 1.0 \AA cost a hefty 1.0 eV, showing that the proposed potential for Si also favours ad-dimer diffusion parallel to the substrate rows, just as for single adatoms. Since the activation energies for interconversion are more than twice that for diffusion and making a crude assumption that the rate of occurrence for both processes exhibits an Arrhenius behaviour, $\omega = A \exp(-\Delta E/k_B T)$ where ΔE is the activation energy, taking a typical prefactor $A \simeq 10^{13}$ Hz [15], the rate of diffusion ($\omega \simeq 2.74 \times 10^3$ Hz, assuming $\Delta E = 0.57$ eV) is 3.5×10^7 times greater than the rate of interconversion ($\omega \simeq 7.76 \times 10^{-5}$ Hz, assuming $\Delta E = 1.02$ eV) at room temperature. We thus conclude that the predominant process occurring at low temperatures is the diffusion of ad-dimers rather than interconversion.

Table 2. Total energy for various values of ψ during interconversion processes: (a) D' dimer \rightarrow F dimer and (b) D dimer \rightarrow B dimer.

(a) ψ (degrees)	Energy (eV)	(b) ψ (degrees)	Energy (eV)
90	-6.51	90	-6.27
75	-6.25	75	-6.08
60	-5.42	60	-5.54
45	-5.54	45	-5.47
30	-5.55	30	-5.25
15	-7.52	15	-5.42
0	-7.95	0	-7.19

But why is diffusion only being observed above the substrate rows and not along the interdimer channels [17]? This may seem surprising at first glance since the activation energy for the latter diffusion is lower. The reason for such a phenomenon can be explained as follows. We have seen earlier [4] that when adatoms become trapped in the F sites, they form 'diluted dimer' structures, comprising of F dimers whose density decays as the temperature is increased. Regular islands can also form at low temperatures by the adsorption and channelling by F dimers of adatoms into the B sites and subsequent formation of B dimers as coverage is increased. Work on this channelling effect is now in progress.

Evidently, the presence of F dimers will give rise to a blocking effect on ad-dimers diffusing along the interdimer channels. In fact, we have found that to cross a F dimer, the D' dimer needs to surmount an energy barrier of ~ 1.0 eV. If the density of F dimers is high (especially at low temperatures), the D' dimers may not even travel far before being blocked and possibly interconverting. As a result, in the time scale of an actual STM experiment, we may not be able to see such diffusion taking place. However at low temperatures the densities of adatoms at the B sites and B

dimers are small. This means that ad-dimers above the substrate rows will not be effectively blocked, making diffusion at larger length and time scales possible.

5. Conclusions

We have reported here a first detailed study of the diffusion and interconversion of Si ad-dimers on the Si(001) 2×1 surface. At low temperatures, ad-dimers are more likely to diffuse along and above the substrate rows rather than in the interdimer channels, as observed for Si clusters experimentally. Diffusion is preferred to interconversion as the activation energy for the latter process is more than twice that of the former. We have also proposed simple mechanisms for ad-dimer migration and interconversion based on an analysis of the corresponding minimum-energy paths. However, care must be taken when extending these discussions to high temperatures since the total energy surface for an ad-dimer can be substantially modified by the high-amplitude vibration of its neighbours. Besides, the results reported here are very potential dependent and their validity lies in the ability of the modified SW potential to model the total energy surface of an ad-dimer on the Si(001) 2×1 surface accurately. The original SW potential, for instance, favoured diffusion of adatoms above the substrate dimer rows [6] while the modified version seems to prefer adatom migration along the side of the dimer rows [4]. So far, ad-dimer diffusion using the original SW potential has not been performed. Perhaps the MD-DFT method proposed a few years ago by Car and Parrinello [16] will be able to explain the dynamical behaviour of ad-clusters on Si surfaces at low or high temperatures with better accuracy.

References

- [1] Stoyanov S 1989 *J. Cryst. Growth* **94** 751
- [2] Miyazaki T, Hiramoto H and Okazaki M 1990 *Japan. J. Appl. Phys.* **29** L1165
- [3] Brocks G, Kelly P J and Car R 1991 *Phys. Rev. Lett.* **66** 1729
- [4] Toh C P and Ong C K 1992 *Phys. Rev. B* **45** 11 120
- [5] Wang Jun and Rockett A 1991 *Phys. Rev. B* **43** 12 571
- [6] Zhang Z Y, Lu Y T and Metiu H 1991 *Surf. Sci.* **248** L250
- [7] Srivastava D and Garrison B J 1991 *J. Chem. Phys.* **95** 6885
- [8] Mo Y-W, Kleiner J, Webb M B and Lagally M G 1991 *Phys. Rev. Lett.* **66** 1998
- [9] Mo Y-W and Lagally M G 1991 *Surf. Sci.* **248** 313
- [10] Dijkkamp D, van Loenen E J and Elswijk H B 1991 *Proc. 3rd NEC Symp. on Fundamental Approach to New Material Phases (1991) (Springer Series of Material Science)* (Berlin: Springer) to be published
- [11] Lagally M G 1992 private communication
- [12] van der Eerden J P, Liu G Z, de Jong F and Anders M J 1990 *J. Cryst. Growth* **99** 106
- [13] Stillinger F H and Weber T A 1985 *Phys. Rev. B* **31** 5262
- [14] Wang S C and Ehrlich G 1990 *Surf. Sci.* **239** 301
- [15] Brocks G, Kelly P J and Car R 1992 *Surf. Sci.* **269-70** 860
- [16] Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471