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## Frustration and (111) silicon surface

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**Résumé.** — Nous montrons que toutes les données expérimentales actuelles sur la surface (111) de Si sont consistantes avec une bande d'énergie des liaisons pendantes ayant une dispersion positive et un dédoublement à cause de l'énergie de corrélation. L'état isolant qui résulte est un état paramagnétique à cause de la frustration pathologique du réseau triangulaire. En l'absence d'ordre antiferromagnétique, l'état fondamental est deux chaînes « zig-zag » de Heisenberg pour la surface (1 × 1) non reconstruite. La reconstruction en enlevant la dégénérescence entre les deux chaînes stabilise la surface (2 × 1), et lui donne un caractère profondément unidimensionnel.

**Abstract.** — Careful analysis of the currently available experimental data on (111) surface of silicon leads us to believe that a positive correlation energy and positive dispersion are responsible for a split surface band of dangling electrons. The resultant ground-state is paramagnetic and insulating but cannot order antiferromagnetically because of the pathological frustration of the triangular lattice. Instead a ground-state results of two correlated zig-zag Heisenberg chains of  $S = \frac{1}{2}$  electrons for the unconstructed (1 × 1) surface. Surface reconstruction, lifts the degeneracy between the two chains, stabilizes the well-known (2 × 1) surface and gives it a pronounced one-dimensional character.

Reconstruction of the dangling bonds on (111) surface of silicon has been object of numerous study [1] because of the fundamental as well as technically important aspect of this surface. In particular the buckling model proposed first by Haneman [2] in which alternate dangling bonds move up or down perpendicular to the surface, transferring the electron from the « down » bond to the « up » and thus creating an energy gap at the surface has enjoyed a great deal of popularity [3]. The Haneman motion of the surface atoms creates a (2 × 1) surface after cleaving and renders the half-filled band of dangling bonds (1 electron/bond) insulating, both facts known experimentally. Recent core-level binding energy shift measurements on the (2 × 1) reconstructed surface, simultaneously by two groups [4, 5] (Himpsel *et al.* and Brennan *et al.*) have shown unambiguously that very little charge transfer is involved between surface atoms (< 0.2 electron/atom). On the other hand in the absence of almost complete charge transfer, the stabilisation of the (2 × 1) surface or the creation of an energy gap at the surface is improbable and this has cast a serious doubt on the Hanemann buckling model. Himpsel *et al.* [6] had suggested that correlation effects between dangling bonds should be invoked to explain suppression of the charge transfer. Recently

in two theoretical papers, Del Sole-Chadi [7] and Northrup-Ihm-Cohen [8] have explicitly taken the correlation energy into account and have concluded that the resultant antiferromagnetic spin-ordering of the (2 × 1) surface allows both for the energy gap as well as the negligible charge transfer observed. These two sets of calculation suffer however from an important oversight : (111) surface of silicon is a triangular lattice and it is known, since the first work of Wannier [9] that *a triangular lattice has no antiferromagnetic ground-state or long-range order*. We must conclude that the energy gaps obtained in these calculations [7, 8] are spurious. In this communication, I would like to indicate the ground-state of the (111) surface of silicon if correlation is important, both of the unreconstructed, as well as of the (2 × 1) surface. The conclusions for the (2 × 1) surface bear some superficial resemblance to the recent chain-model of Pandey [10].

Our starting point is the tight-binding Hubbard [11] Hamiltonian for the surface atoms

$$H = \sum_i \varepsilon_0 n_{i\sigma} + \sum_{i \neq j} t_{ij} C_{i\sigma}^* C_{j\sigma} + U \sum n_{i\sigma} n_{i-\sigma}, \quad (1)$$

where the  $i$ 's refer to the surface sites,

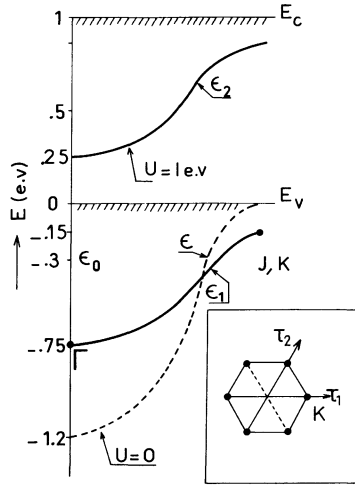


Fig. 1. — Dispersion relationship  $\varepsilon_{1,2}(k)$  of the unreconstructed  $(1 \times 1)$  (111) silicon surface,  $\varepsilon_1$  lower Hubbard-band,  $\varepsilon_2$  upper Hubbard-band, with positive correlation energy  $U = 1$  eV,  $\varepsilon_0 = -0.5$  eV and  $t_1 = 0.15$  eV; uncorrelated surface band  $\varepsilon(k)$  with  $U = 0$ . The inset shows the primitive translation vectors  $\tau_1$  and  $\tau_2$  for the triangular lattice. Zero of energy is maximum of the bulk valence band  $E(\Gamma_{25})$ .

$\varepsilon_0$  ... site energy of the dangling bond at any site  $i$ ,  $t_{ij}$  refers to the transfer integral between near-neighbour sites (we shall consider  $\pi$ -integrals only);

$U$  ... the on-site Coulomb repulsion between two opposite spin electrons; \*

$C^*$ ,  $C$  are creation and destruction operators for spin  $\sigma$ ,  $n_{i\sigma}$  ... number operator.

For  $(1 \times 1)$  (111) surface, using  $\tau_1$  and  $\tau_2$  as two primitive lattice translation vectors (Fig. 1 inset), we get for the dispersion, if  $U = 0$ , as

$$\varepsilon_k = \varepsilon_0 - 2 t_1 [\cos k_1 a_0 + \cos k_2 a_0 + \cos(k_1 - k_2) a_0] \quad (2)$$

where :

$a_0$  ... distance between two dangling bonds,

$t_1$  ... near-neighbour transfer integral,

$k_1$  and  $k_2$  are wave-vectors along  $\tau_1$  and  $\tau_2$  directions.

For  $U \neq 0$ , the approximate Hubbard [11] solution gives us the two Hubbard-bands  $\varepsilon_1(k)$  and  $\varepsilon_2(k)$  as the two roots of the equation

$$[E - \varepsilon_k][E - \varepsilon_0 - U] + n_{-\sigma} U(\varepsilon_0 - \varepsilon_k) = 0. \quad (2a)$$

Note that the Hubbard gap obtained here is quite different from the antiferromagnetic gap assumed in references [7] and [8] which is in reality a Slater gap. No spin periodicity is assumed and a paramagnetic ground-state is retained. For a paramagnetic ground-state  $n_{-\sigma} = n_{\sigma} = \frac{1}{2}$ , in case of 1 electron/atom. Equation (2) as well as the solutions of (2a) are displayed in figure 1 for the following choice of parameters.

$$\left. \begin{array}{l} \varepsilon_0 = -0.3 \text{ eV} \\ t_1 = 0.15 \text{ eV} \\ U = 1 \text{ eV} \end{array} \right\} \text{ (see footnote (1)).}$$

The zero of energy is chosen as the maximum of the valence band at the  $\Gamma_{25}$  point.

We note from figure 1, that the effect of  $U$  besides rendering the half-filled surface-band develop an energy gap, also narrows the band (band-width goes from  $8 t_1$  to  $4 t_1$ ). The lower Hubbard-band ( $\varepsilon_1(k)$ ) corresponds to a correlated spin fluid, with a total dispersion of  $\sim 0.6$  eV. We may note the following features of figure 1 :

$$(E_{\Gamma} = \varepsilon_0 - 3 t_1 = -0.75, \quad E_{\mathbf{K}} = E_{\mathbf{J}} = \varepsilon_0 + t_1 = -0.15).$$

(a) The lower Hubbard-band disperses upward from  $\Gamma$  at  $-0.75$  eV to J point at  $-0.15$  eV. Recent photoemission experiments [6, 12] are in very good agreement with these results.

(b) The Mott-Hubbard gap is  $E_{\text{H}} = U - 4 t_1 = 0.4$  eV. Since this corresponds to single-particle excitation, this would represent the optical peak at  $\sim 0.45$  eV observed by Chiarotti *et al.* [13].

(c) Finally the Fermi-level of the surface-band, in case of  $n$ -type silicon, will shift to accommodate excess charge from bulk from  $\varepsilon_0 + U/2$  to the upper Hubbard-band at around 0.25 eV from the valence band and will remain pinned there due to the large density of states available. While the Fermi-level pinning at the silicon surface is well-known, the upward shift was observed by Wagner *et al.* [14] by photoemission.

(1) The  $t_0$  value was taken from the tight-binding calculations of Ciraci *et al.* [21]. The position of this level is very sensitive to the crystal potential and local environment.

The  $t_1$  value for the  $\pi$ -electrons (0.15 eV) was obtained from  $t_1^0$  as  $t_1^0 \sim \frac{1}{4} \Delta E_p$  where  $\Delta E_p$  is the width of the bulk silicon p-band ( $E_{\Gamma_{25} v} - E_{X_4 v}$ ) known experimentally to be  $\sim 3.2$  eV, and exponentially scaling down  $t_1^0$  from the bulk distance of 2.35 Å to inter-dangling bond-distance of 3.85 Å, on the (111) surface. An approximate estimate for the correlation energy  $U$  can be obtained from

$$U = \frac{e}{K} \int_{\text{volume}} a^2(1) a^2(2) \frac{1}{r_{12}} dv_1 dv_2$$

where :

$e$  is the charge on the electron

$K$  static dielectric constant of silicon

$a(1)$  and  $a(2)$  are the wave-functions of the two electrons on the dangling bond separated by a distance  $r_{12}$ . Writing for the localized wave-functions  $a(r) = \left(\frac{\alpha^3}{\pi}\right)^{1/2} \exp(-\alpha r)$  where  $\alpha$  is the localization parameter. The integral, as calculated by Slater [22] is  $U = \frac{51^2 \alpha}{8 K}$ .

From the value of  $\alpha$ , estimated from the Harrison relationship [23] for silicon, we obtain  $U \sim 1$  eV.

The electrons in the paramagnetic insulating state, as represented by the band  $\epsilon_1(k)$  in figure 1 are subjected to the antiferromagnetic Heisenberg interaction given by the Hamiltonian

$$H_A = \sum_i 2 J_{ij} \sigma_i \sigma_j \quad (3)$$

where :

$J_{ij} = 2[t_{ij}]^2/U$  is the Anderson [15] kinetic exchange,  $\sigma_i^z$ 's are spin operators for  $\frac{1}{2}$  spin electrons at site  $i$ .

This means that the electrons in the paramagnetic lower Hubbard-band of figure 1 can lower their energy if the spins can order. But since the triangular lattice is completely frustrated, the antiferromagnetic Ising ground-state having no long-range order as Wannier [9] showed, has large degeneracy and a finite entropy. The best that the Ising spins can do (i.e. in the absence of  $J_x$  and  $J_y$  components of the exchange) is as shown in figure 2, where the frustrated spins are arranged in plaquettes, and each triangle has at least two antiferromagnetic interactions, the so-called short-range ordered (S.R.O.) states. If the interaction is purely Ising, the ground-state energy is  $E_{\text{Ising}}/N = 0.5 J$  where  $N$  is the number of lattice sites and  $J$  is the Z-part of the exchange interaction  $J_{ij}$ . What happens to these localized spins if X and Y interactions are turned on, i.e. when they are allowed to tunnel ?

We can rewrite the isotropic Heisenberg Hamiltonian (3) in the following way :

$$H = 2 J \sum_i \sigma_i^z \sigma_j^z + J \sum_{i,j} (\sigma_i^+ \sigma_j^- + \sigma_j^+ \sigma_i^-). \quad (4)$$

Fazekas and Anderson [16], parametrizing the second term of the Hamiltonian (4) as a small first-order perturbation on the Ising ground-state (i.e. interchange of pair of electrons that leave S.R.O. unchanged), concluded that the Ising state is unstable to the formation of a small number of mobile paired electrons, the so-called « resonating valence bonds ». If one goes beyond the first-order perturbation and considers electron interchange, that induces breaking of S.R.O. (e.g. interchanging spins 1 and 2 in Fig. 2, four antiparallel pairs in a given hexagon are replaced by parallel ones, with a resultant excited state higher by  $2 J$  than the Ising energy), we need to calculate the correction to the Ising energy, at least to second-order, and we thus obtain

$$\tilde{E}_0 = E_{\text{Ising}} - 2 N \frac{J^2}{4 J} = - N J \quad (5)$$

where  $H^\pm$  acts on  $2 N$  antiparallel pairs.

We note  $\tilde{E}_0$  can only be an over-estimate to the ground-state energy; for at best  $H^\pm$  can bring about formation of zig-zag Heisenberg chain  $\alpha$  (in Fig. 2) whose ground-state energy is known exactly [17]. It is  $E_0 = 0.887 6 N J$ . This ground-state is not antiferromagnetic and resembles « liquid » diamagnetic pair bonds. We can conclude that a zig-zag spin-chain like  $\alpha$  in figure 1 could represent a ground-state to the triangular antiferromagnetic Heisenberg lattice. We further note that if  $\alpha$ -chain results from flipping spins 1 and 2 etc.,  $\beta$ -chain (Fig. 2) is also an exactly equivalent Heisenberg chain, related by translation operator  $\tau$

$$\tau |\alpha\rangle = |\beta\rangle, \quad \tau |\beta\rangle = |\alpha\rangle, \quad (6)$$

where  $|\alpha\rangle$  and  $|\beta\rangle$  denote wave-functions of the  $\alpha$  or  $\beta$ -chain.

The correct ground-state then must be either

$$\Psi^+ = |\alpha\rangle + |\beta\rangle \quad \text{or} \quad \Psi^- = |\alpha\rangle - |\beta\rangle \quad (6a)$$

with

$$H\Psi^+ = E_0 \Psi^+, \quad H\Psi^- = E_0 \Psi^-, \quad (6b)$$

where  $E_0$  is the energy of any of the Heisenberg chains  $\alpha$  or  $\beta$ .

We conclude that for a  $(1 \times 1)$  (111) surface of silicon, the triangular lattice resonates between  $\alpha$  and  $\beta$  chains, in  $\Psi^+$  and  $\Psi^-$  states. This leads us to believe that the ground-state of antiferromagnetic Heisenberg triangular lattice are two correlated Heisenberg chains. It is worthwhile noting that the one-dimensional antiferromagnetic Ising chain [18] has exactly the same ground-state energy ( $0.5 J/\text{atom}$ )

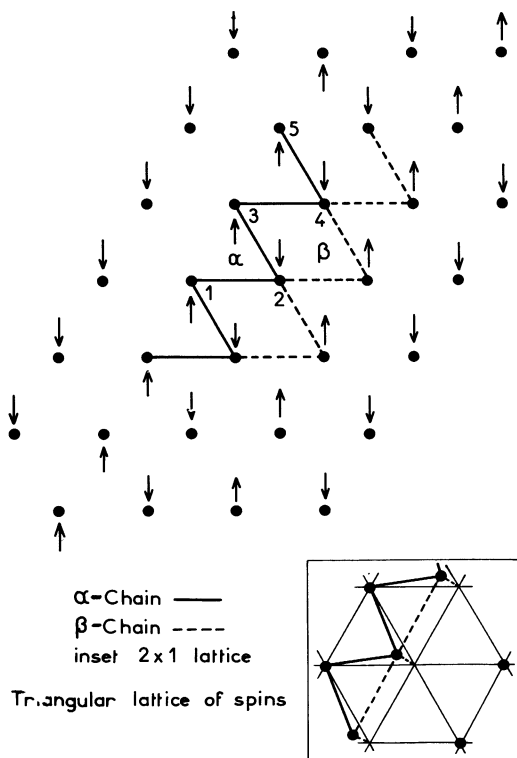


Fig. 2. — Triangular frustrated antiferromagnetic lattice of spin  $\frac{1}{2}$ ; formation of equivalent zig-zag Heisenberg chains  $\alpha$  and  $\beta$  for  $(1 \times 1)$  surface. Inset corresponds to  $(2 \times 1)$  surface, with atom displacement of  $0.1 \text{ \AA}$  on alternate line of atoms.

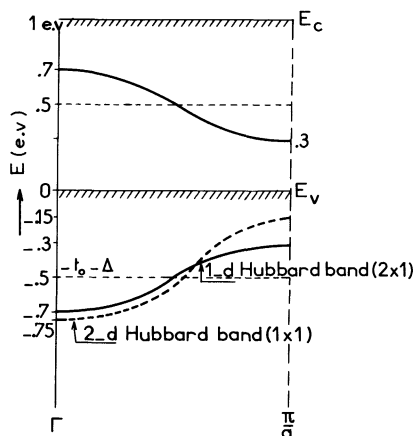


Fig. 3. — (—) The two one-dimensional Hubbard-bands of the  $(2 \times 1)$  silicon surface, with  $\Delta = 0.2$  eV and  $t_1 \sim 0.2$  eV; (---) unreconstructed  $(1 \times 1)$  lower surface Hubbard-band shown for comparison.

as the triangular antiferromagnetic Ising net [9], consequence of frustration.

$(2 \times 1)$  surface would result if the translational symmetry and hence equivalence between  $\alpha$  and  $\beta$  chains is lost, as due displacement, shown in the inset of figure 2. As the two-dimensional electrons localize themselves on a given chain, the increase of kinetic energy (correlated lower Hubbard-band width  $\sim 2 t_1$  as against  $4 t_1$ ) has to be compensated by the deformation potential shift of the dangling bond site energy (from  $t_0$  to  $t_0 - \Delta$ ) due to site displacement. The resultant  $(2 \times 1)$  dispersion curve is shown in figure 3 for a  $\Delta \sim 0.2$  eV [19] for a displacement of  $0.1 \text{ \AA}$  with a slightly increased  $t_1 = 0.2$  eV. The two one-dimensional Hubbard-bands has a dispersion width  $\sim 0.4$  eV each and the lower Hubbard-band is full. We note the large density of states at the edges of these Hubbard-bands, characteristic of one-dimensional systems; those at  $\pi/a$  of the upper Hubbard-band could well be responsible for Fermi-level shift seen on Si(111) surface if called upon to accommodate excess electronic charge from bulk [14]. Besides these single-particle excitation spectrum, measurement of the one-dimensional spin-wave excitation [18] as well as magnetic susceptibility will be a crucial test of this model (Fig. 4). The spin-wave state of figure 4 is not the same as that of a conventional antiferromagnetic spin-wave; in particular it is gapless (at  $k = 0$ ) in its collective excitation spectrum.

The zig-zag chain proposed here for the  $(2 \times 1)$  surface bears only a superficial resemblance to the  $\pi$ -bonded chain recently proposed by Pandey [10] and which is unlikely for at least two related reasons.

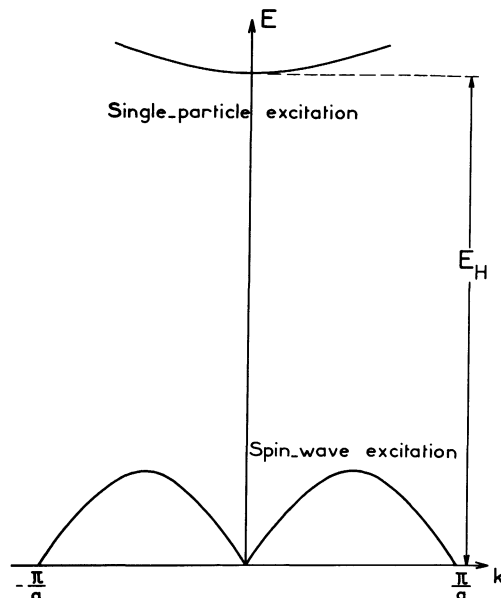


Fig. 4. — Collective spin excitation spectrum and single particle excitation spectrum of the zig-zag Heisenberg chain;  $E_H$  refers to the Hubbard gap. Undimerised chain.

(a) It is hard to see the driving force for the  $\pi$ -bonded chain formation considering that the  $\frac{1}{2}$  filled two-dimensional band, without correlation (Fig. 1,  $U = 0$ ) has a band-width  $8 t_1$  while the single  $\pi$ -band is only half as wide. On the other hand a band narrowed by correlation and electrons more localized will be susceptible to strong electron-phonon coupling.

(b) In the most recent communication [20], Pandey dispensed the buckling model for its neglect of the correlation energy which he calculated to be large that is in turn neglected to arrive at the  $\pi$ -bonded chain.

In conclusion, I have shown that the currently available experimental data on (111) surface of silicon is consistent with a surface dangling bond band split by strong correlation with positive dispersion, that the resultant insulating paramagnetic state because it is frustrated in the triangular lattice to order antiferromagnetically goes to a ground-state of two correlated zig-zag Heisenberg chains. Lattice deformation, by lifting the degeneracy between these two chains stabilizes a  $(2 \times 1)$  surface<sup>(2)</sup>.

<sup>(2)</sup> Since this article was submitted for publication, two recent communications by Duke-Ford [24] and Lanoo and Allan[25] that treat correlation have been brought to the author's attention.

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