

## Comment on "Kinetics of the hydrogen chemisorption process for Nb"

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We reanalyze a recent paper by Kim *et al.* [Phys. Rev. B **38**, 5716 (1988)] regarding the kinetics of hydrogen uptake by niobium surfaces. We show that the kinetic analysis performed by these authors is incorrect.

In a recent paper Kim *et al.*<sup>1</sup> address the problem of the kinetics of hydrogen uptake by niobium surfaces and claim to solve an earlier apparent controversy between Lagos, Martinez, and Schuller<sup>2,3</sup> and Dienes, Strongin, and Welch.<sup>4</sup> A Comment is in order since the work of Kim *et al.* fails to address the central issue of the problem, is technically incorrect, and yields misleading conclusions.

The interaction of hydrogen with transition-metal surfaces is a problem that has received considerable theoretical and experimental attention. The problem can be divided into two general categories: energetics and kinetics. Particularizing the problem of the energetics to the surface of niobium, it is found experimentally that there are two or more different states in which hydrogen is bound to the surface.<sup>5-8</sup> These states, observable by photoemission, have been shown experimentally to be due to hydrogen bonded close to the exposed surface, possibly one or more of them residing below the surface. Angle-resolved photoemission measurements have shown clearly the bonding of hydrogen to subsurface sites and similar conclusions were reached for the Pd(110) (Refs. 9 and 10) and Cu(110) (Ref. 11) surfaces from atomic scattering, low-energy electron diffraction and high-resolution electron-energy-loss spectroscopy studies. The presence of subsurface bonded hydrogen was also found for the Pd(111) surface using the embedded-atom method<sup>12</sup> and self-consistent pseudopotential calculations.<sup>13</sup> A natural explanation for these subsurface states has emerged from an earlier theory which takes into account the interaction of the hydrogen atom with the surface lattice vibrations, a surface-polaronic effect.<sup>14,15</sup>

After hydrogen fills an interstitial site, the crystal ions surrounding it move in order to minimize the total energy. This energy reduction, of elastic origin, is quite significant and is enhanced by the presence of a surface, where the crystal ions are freer to move.<sup>14,15</sup> Calculations of the surface contribution to the self-trapping energy of hydrogen impurities in several metals predicted a variety of effects,<sup>2,14-16</sup> which was subsequently observed by experiments.<sup>8-11</sup> These subsurface traps were found to be particularly strong in niobium.<sup>15</sup> Theoretical estimates

of the energy of a hydrogen in an interstitial site just below the Nb (110) surface gives values lower by at least 0.1 eV, than the hydrogen atom chemisorption energy.<sup>15</sup> Therefore the subsurface hydrogen layer is most stable in niobium, and has a large activation temperature  $T_c$ . It seems, therefore, that the presence of subsurface states is on firm footing, both experimentally and theoretically.

The theoretical situation with the kinetics of hydrogen absorption is more controversial. Two differing viewpoints have been expressed. Dienes, Strongin, and Welch<sup>4</sup> presented a kinetic model in which the bulk hydrogen absorption is controlled by the presence of two surface states which are caused by electronic effects and which control the kinetics.<sup>17</sup> On the other hand, as a consequence of the existence of subsurface states, Lagos, Martinez, and Schuller<sup>2</sup> presented a calculation which takes into account the activated transfer of hydrogen from the gas phase, through the chemisorption and subsurface sites, to the bulk. The models of Dienes, Strongin, and Welch and Lagos, Martinez, and Schuller at high temperature both reduce to a two phases model advanced earlier by Pick *et al.*<sup>18</sup> In this model the surface coverage  $\theta_a$  (given by the chemisorption) and the bulk concentration  $x$ , for vanishing external  $H_2$  pressure, are related by the equilibrium equation<sup>2</sup>

$$\frac{\theta_a}{1-\theta_a} = \frac{\beta}{\nu} \frac{x}{1-x}, \quad (1)$$

where  $\beta$  and  $\nu$  are model dependent and have an activated behavior. At low temperature, however, the two models depart. Dienes, Strongin, and Welch suggest the presence of a surface hydride, which modifies the kinetics because of the strong interactions between hydrogens and the formation of clusters. Lagos, Martinez, and Schuller conclude, on the other hand, that at low temperature the subsurface layer of interstitial sites (even for small values of  $x$ ) is filled by very stable hydrogen states, thus playing the role of a subsurface valve which disconnects the chemisorbed layer from the bulk, at temperatures below  $T_c$ . This follows as a natural consequence of the theoretical estimates for the surface enhanced self-trapping

effect,<sup>14,15</sup> which turns out to be particularly strong in niobium. The basic ideas behind the two proposed models are, however, nonexclusive. It may even be that the situation requires the inclusion of both effects.

The experimental situation has been studied quite extensively, starting with the work of Smith,<sup>5,19</sup> almost a decade ago. He showed that, on exposing a clean niobium sample at  $T > 400$  K to  $H_2$  atmosphere,<sup>19</sup> the surface coverage  $\theta_a$  and bulk hydrogen concentration  $x$  evolve as predicted by the kinetic model of Pick *et al.*<sup>18</sup> Furthermore, placing the hydrogen loaded sample in vacuum the values of  $\theta_a$  and  $x$  follow the simple equilibrium law (1), for any temperature in the range  $400 \text{ K} < T < T_d$ , where  $T_d$  is the desorption temperature. The important point, however, is that this simple picture fails when  $T < 400$  K. In this range of temperatures, the surface coverage  $\theta_a$  grows much faster than expected from the model of Pick *et al.*, reaches the same maximum coverage  $\theta_m$  for all temperatures and  $H_2$  pressures, and becomes independent of the bulk concentration  $x$ . Smith shows that in this regime the solution<sup>19</sup>

$$\theta_a(t) = \frac{2fst}{1 - 2fst} \quad (2)$$

of the kinetic equation

$$\frac{d\theta_a}{dt} = 2fs(1 - \theta_a)^2, \quad (3)$$

where  $f$  is the number of  $H_2$  molecules impinging on the surface per unit time and per chemisorption site, and  $s$  is the initial sticking coefficient, fits the data very well. Equation (3) corresponds to second-order sticking without leak to the gas phase nor the bulk. Hence at  $T < 400$  K the chemisorbed and bulk phases become decoupled.<sup>19</sup> Moreover, Smith's data clearly show that the photoemission intensity is strongly photon-energy dependent.<sup>5</sup> The photoelectron spectrum characteristic of the surface (or subsurface) hydrogen grows very quickly for  $h\nu = 21.2$  eV; however, a much slower growth is obtained for  $h\nu = 11.8$  eV. Since the hydrogen absorption cannot be photon-energy dependent, these results indicate that further theoretical work regarding the significance of photoemission intensity is necessary before the photoemission data can be directly compared with hydrogen absorption models.<sup>3</sup> Smith's early interpretation,<sup>5</sup> however, relating this effect with finite escape depths in photoemission and the hydrogen filling of subsurface layers, seems confirmed by the subsequent history of the problem, summarized in the preceding paragraphs. Recent angle-resolved photoemission work lends further support for the existence of a model involving the sequential exchange of hydrogen between two sites close to the surface at low temperature and the depletion of hydrogen from both surface and subsurface sites at high temperature.<sup>8</sup>

With this background the work of Kim *et al.*<sup>1</sup> is flawed for the following reasons.

(i) They postulate two different hydrogen chemisorption states located in the same sites, leading to a complicated set of kinetic equations. Subsequently, they assume thermal equilibrium between the populations of these two classes of surface states.<sup>1</sup> This makes the distinction between them unnecessary, since what matters under the equilibrium hypothesis is only the total population  $\Theta = \theta_a + \theta_b$  of the two types of chemisorbed states.

(ii) The kinetic equation relating the total coverage  $\Theta$  and bulk concentration  $x$  [Eq. (3) of Kim *et al.*] is oversimplified by neglecting all the terms proportional to  $x$ .<sup>1</sup> Simple energy considerations imply that  $K_\beta \gg v_A/\alpha$ , which explains why a small bulk concentration can equilibrate a finite surface coverage. Thus it is not obvious that Eq. (4) of Kim *et al.* follows directly from Eq. (3) of the same authors,<sup>1</sup> even assuming  $x \ll 1$ . Furthermore, and principally, the authors<sup>1</sup> fail to realize that each of the two terms containing  $x$  in their Eq. (3) are in general much larger than the sticking term  $2fS_0K_{di}(1-\Theta)^2$ , and only the sum  $K_\beta x(1-\Theta) - (1-x)v_A\Theta/\alpha$  may be comparable with the sticking rate. Dropping one of the two terms in  $x$  constitutes a gross error. Equation (7) of Ref. 1 is flawed for the same reason.

(iii) Kim *et al.* solve correctly their incorrect Eq. (4).<sup>1</sup> The equation is a first-order differential equation whose solution is fully determined by the condition  $\Theta(0) = 0$ . However, they introduce artificially a finite saturation time  $t_m$  and a saturation coverage  $\Theta_m$  different from the asymptotic value  $\Theta(\infty)$ .<sup>1</sup> The idea of the saturation time and coverage, certainly erroneous, introduces new parameters which are used to compensate approximately the error incorporated in the starting equation.<sup>1</sup>

(iv) The comparison of model kinetic calculations with experimental data for only  $T = 300$  K is of little use. The fit to the experimental data fails at low and high exposure levels, is worse for higher pressures and it only fits reasonably well at intermediate exposure. Under these circumstances, a quantitative comparison between different models as far as quality of fit to experiment is necessary before one or the other model is selected as the correct explanation of the data.

(v) Quantitative comparisons with the photoemission data should take into account the points discussed in Ref. 3 relative to the dependence of the hydrogen-induced photoemission peak on the energy of the incident photons. In addition, the temperature of the various surface (or subsurface) states as found experimentally and described above should be addressed and cannot be ignored.

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