Surface defects and the collective nature of diffusion in the system Li–W (011)

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The effect of a small number of artificially created defects (adsorbed oxygen) on the surface diffusion and lithium on the (011) face of W is investigated. The data obtained indicate the collective nature of the diffusion. The results are discussed using the soliton mechanism of diffusion.

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When the deviation of the concentration of adsorbed atoms (adatoms) from the stoichiometric value, corresponding to the two-dimensional crystal commensurable with the substrate, is small, a superlattice of solitons (domain walls) can be formed in this crystal.[1,2] Solitons are linear regions of compression or stretching of the film, whose width is determined by the adatom lateral interaction energy and the potential relief of the substrate. On the basis of experimental data,[3] it was proposed in Ref. 4
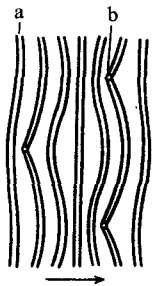
FIG. 1. Deformation of the soliton lattice in the case of pinning by defects. The arrow indicates the direction of diffusion: (a) soliton; (b) defect.

that the solitons can carry mass in the process of surface diffusion, giving it a specific collective character.

A separate soliton is located in a potential relief, which is analogous to the Peierls relief for dislocations[5,6] (regime of pinning by the substrate). This situation remains up to some critical distance between solitons, at which their superlattice "tears away" from the Peierls relief. On an ideal substrate, this would lead to activationless transport of mass by solitons, but in the presence of surface defects, which pin solitons (Fig. 1), diffusion in this case will have an activation character (regime of pinning by defects). The activation energy in this case must be determined by the energy required to separate a soliton from a defect. In the case that the defects are strongly bound to the substrate, the activation energy will be of the order of the rupture energy of a soliton and, in addition, it will not depend on the concentration of defects and will be insensitive to their nature.

The concentration gradient of adatoms in the film leads to a pressure gradient in the elastic soliton lattice. As a result, an additional force in the direction of diffusion acts on a soliton at the point that it is pinned to a defect. As the concentration of defects decreases, the magnitude of this force increases. This means that the probability for separation from a defect also increases, thereby increasing the diffusion coefficient D. Since the activation energy does not change, the increase in D must occur due to the preexponential factor D_0.

In order to check these theoretical predictions,[4] in this work we studied the dependence of the coefficient of diffusion in a two-dimensional crystal near the point of commensurability as a function of the concentration of artificially created surface defects. We studied the diffusion of lithium on the (011) face of tungsten, on which the defects were formed by adsorbed oxygen adatoms. At the temperatures of the experiment, the diffusion coefficient of oxygen is approximately 10 orders of magnitude lower than that of lithium,[7,8] so that oxygen adatoms can be viewed as nearly stationary defects. The coverage of the surface by oxygen θ_k was controlled by the temperature T_n at which the crystal, covered beforehand by oxygen, was heated. The quantity θ_k was estimated from the change in the work function. The investigations were carried out with θ_k indicated in Fig. 2.

The procedure for studying surface diffusion is described in Refs. 3 and 9. The diffusion was investigated with a single layer coating of lithium $\theta = 1$, with which a $C(1 \times 1)$ structure, commensurable with the substrate, is formed.[9] Figure 2 shows the temperature dependences of the diffusion coefficient $D = D_0 \exp(-E_d/kT)$ (Arrhen-
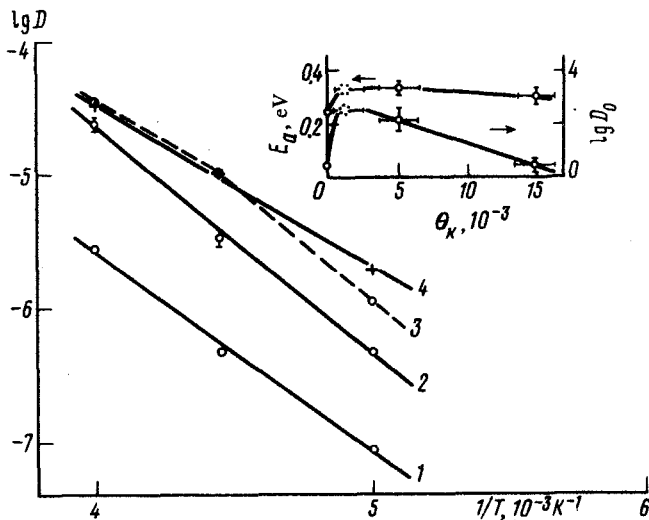
FIG. 2. Arrhenius straight lines for diffusion of lithium with different coatings of oxygen. (1) $\theta_k \simeq 0.015$, T_n = 1900 K; (2) $\theta_k \simeq 0.005$, T_n = 1950 K; (3) $\theta_k \simeq 0.001$, T_n = 2000 K; (4) $\theta_k = 0$, T_n = 2300 K, ($\theta_k = 1$ corresponds to an oxygen adatom concentration equal to 14.1×10^{14} cm^{-2}). The insert in the upper right-hand corner shows E_d and D_0 as a function of θ_k. D and D_0 are in units of cm^2 s^{-1}.

ius straight lines) for different values of θ_k. The values of D_0 and E_d calculated for them are shown in the insert in Fig. 2 (for $\theta_k \lesssim 0.001$, data related to the low-temperature region are presented). When θ_k decreases from 0.015 to 0.001, the quantity E_d remains constant within the range of accuracy of the experiment, while D_0 increases by two orders of magnitude. It is interesting that even with $\theta_k \lesssim 0.001$, the coefficient of diffusion for low values of T is much lower than on a clean surface, although for high values of T, a transition is already observed to parameters characteristic of a clean surface (straight line No. 4). "Characteristic" defects, namely, steps, vacancies, and so on, play the role of stoppers on an oxygen-free surface, so that in different temperature intervals of curve 3 in Fig. 2, the values of E_d and D_0 are apparently determined by different types of stoppers.

The characteristic surface defects, in principle, could lead to a nonuniform distribution of oxygen adatoms on the surface, for example, accumulation of oxygen adatoms at steps representing linear defects. However, data from structural studies[10] show that this effect is quite weak. Estimates based on data on the difference of the heats of adsorption of oxygen on the steps and on terraces[11] and on the diffusion coefficient of oxygen on W (011) lead to the same conclusion.[7,8]

Thus, strong changes in D_0 are caused by oxygen adatoms whose concentration is a factor of 10^2–10^3 lower than that of diffusing lithium atoms; these adatoms are situated at distances of at least 10–15 lattice constants. This fact supports the model, according to which diffusion in the system studied has a collective character. The dependences of E_d and D_0 on the defect concentration agree with the predictions of the theory[4] of the soliton mechanism of surface diffusion.

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