Surface Self-Diffusion of Atoms and Atom Pairs*

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Quantitative observations have for the first time been made of the surface diffusion of single self-adsorbed tungsten atoms and atom pairs. Measurements on the (211) plane indicate that motion of single atoms is normal, occuring over a barrier of 74 kJ/mole, with a pre-exponential factor $D_0 = 10^{-3}$ cm^2/sec. Motion of pairs formed by atoms in adjacent [111] channels is highly correlated; it involves a much smaller barrier, 28 kJ/mole, and a pre-exponential factor of only 10^{-12} cm^2/sec.

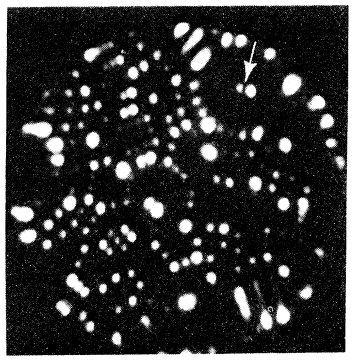
Recent measurements on the diffusion of rhodium atoms self-adsorbed on the rhodium lattice have revealed a most surprising behavior.[1] When two atoms were placed on a (110) plane, strong correlations were found in the motion of the two, extending to interatomic separations larger than 7.5 Å. These qualitative observations immediately raise the question: How significant are interatomic correlations in affecting the quantitative surface-diffusion characteristics of atoms adsorbed on their own lattice?

This study was undertaken to establish quantitatively the diffusion behavior of single adatoms, compared to that of adatoms in interaction with others. For this we have selected the (211) plane of tungsten. A most unusual diffusion behavior has previously been reported on the (211) plane.[2,3] In contrast with the (110) and (321) planes, the other two planes of the tungsten lattice for which data are available, motion was characterized by a very low activation energy (51.4 kJ/mole), as well as a pre-exponential term D_0 four orders of magnitude below normal. The structure of this surface is similar to that of the (110) plane of the fcc lattice, on which correlation effects have been found to play a significant role. In the [111] direction, the (211) plane is made up of close-packed rows of atoms; these form channels 4.47 Å wide along which diffuse the self-adsorbed atoms. By analogy with the qualitative behavior observed on the (110) plane of the fcc lattice, strong correlations should be expected between atoms moving in separate channels on the (211) plane of tungsten.[4]

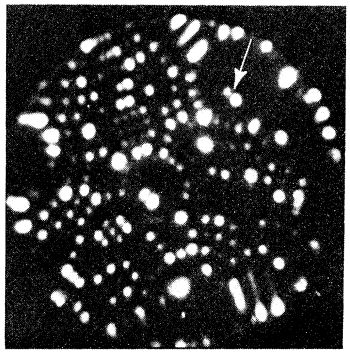
Measurements on single atoms and on atom pairs have been made by standard methods.[2] For the former, a single tungsten atom is deposited on a (211) plane by evaporation from a hot filament. Its positions are observed at 15°K in a field-ion microscope,[5] after successive diffusion periods at an elevated temperature. The diffusion coefficient D is then obtained from

$$D = Nl^2/2\tau.$$

Nl^2, the product of the number of atomic jumps N during the diffusion interval τ and the mean square jump distance l^2, is derived from the spa-



(a)



(b)

FIG. 1. Field-ion micrographs of a [111]-oriented tungsten surface prepared by field evaporation at 15°K. (a) Arrows indicate pairs of tungsten adatoms on {211} planes, with atoms in adjacent ⟨111⟩ channels; (b) the same surface after thriteen diffusion intervals at 275°K. The pairs have moved over the {211} planes without dissociation.

tially averaged mean square displacement $\langle\langle R^2\rangle\rangle$, the quantity accessible to experiment,[6] through

$$\langle\langle R^2\rangle\rangle \approx Nl^2[1 - \tfrac{4}{3}a(2Nl^2/\pi)^{1/2}];$$

a is the length of the channel along which diffusion occurs. To characterize the behavior of atom pairs, two atoms are deposited on a plane, one each in adjacent channels; in all other ways the analysis proceeds just as above.

That motion of two tungsten atoms in adjacent channels of the (211) plane is correlated appears from the sequence in Fig. 1. In the first observation the two atoms are in close proximity to each other. After thirteen diffusion intervals of 60 sec each at 275°K, the distance between them has hardly changed even though the pair as a unit has undergone a significant displacement. The effect of temperature upon the diffusion is shown in Fig. 2, both for single tungsten atoms on the (211) plane, and for two atoms in neighboring channels. In the usual representation of the diffusion coefficient, $D = D_0 \exp(-V_D/kT)$, there is a very significant difference in the barrier V_D for the motion of single atoms and for that of pairs. For single atoms, the activation energy amounts to 74 kJ/mole; for pairs it is only 28 kJ/mole.[7] Equally dramatic are the differences in the pre-exponential term D_0: 10^{-3} cm^2/sec for single atoms, and 10^{-12} cm^2/sec for pairs. The former is entirely normal, and consistent with atomic jumps involving essentially zero entropy of activation.

Single-atom diffusion over planes of the body-centered cubic lattice therefore appears to occur with entirely normal diffusion dynamics, just as on a face-centered cubic crystal.[1] The anomalous behavior previously observed on the (211) plane of the bcc lattice, and attributed to cooperative effects involving the lattice,[8] have in these experiments been identified as resulting from correlations between adatoms on the same surface. These correlations are of considerable importance in their own right, and it will be interesting to explore more fully the atomic dynamics which result in such a remarkably low barrier and pre-exponential factor in the diffusion of atom pairs.

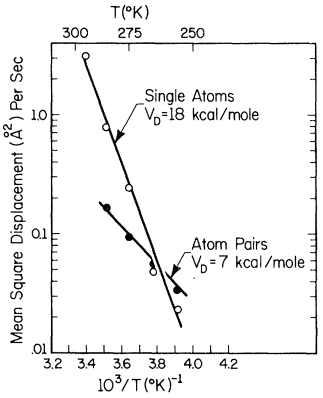


FIG. 2. Temperature dependence of surface self-diffusion for single tungsten atoms and atom pairs on the (211) plane of tungsten. Pairs consist of atoms in adjacent rows. For single atoms, $D_0 = 10^{-3}$ cm^2/sec; for pairs, $D_0 = 10^{-12}$ cm^2/sec.

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[1]G. Ayrault and G. Ehrlich, to be published.

[2]G. Ehrlich and F. G. Hudda, J. Chem. Phys. 44, 1039 (1966).

[3]D. W. Bassett and M. J. Parsley, J. Phys. D: Appl. Phys. 3, 707 (1970).

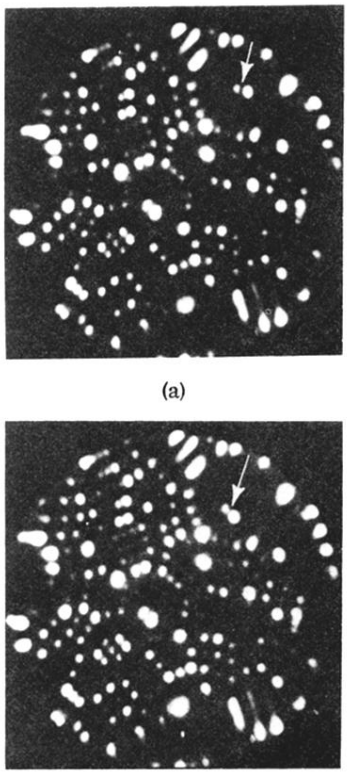
[4]Qualitative indications of correlated motion on this plane have been reported by T. T. Tsong, Phys. Rev. B 6, 417 (1972).

[5]E. W. Müller and T. T. Tsong, *Field-Ion Microscopy* (American Elsevier, New York, 1969).

[6]G. Ehrlich, J. Chem. Phys. 44, 1050 (1966).

[7]Absolute barrier heights are based on a preliminary temperature calibration.

[8]G. Ehrlich and C. F. Kirk, J. Chem. Phys. 48, 1465 (1968).



(a)

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