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# Mass Spectrometric Investigations of the Alkali Migration on Tungsten at Low Coverages

The surface diffusion for five alkali metals on polycrystalline tungsten and ionic thermal desorption are studied by a method based on the alkali ion current noise arising from the fluctuation of the work function as a result of random fluctuations of the alkali adsorbate density.

The activation energy for surface diffusion for Li, K, Rb and Cs have been determined by measuring the spectral density functions and their parameters.

## METHOD

The method is based on the relationship between the number $n$ of adatoms adsorbed on a small region of the ions emitter and the ion thermoemission current $i$ emitted from this region.

Due to random surface migration of adatoms, $n$ undergoes fluctuations $dn$ around its mean value. These fluctuations are reflected in current fluctuations $di$, with a spectral density $S$: $S = \langle di^2 \rangle / df$, [1].

The mean square of the ion current fluctuations is given by:

$$\langle di^2 \rangle = i_0^2 (\Pi e \ \mu / \xi_0 k T l)^2 n_0 D \tau_0, \tag{1}$$

where $i_0$ is the DC ion current intensity, $\mu$ — the dipole moment of the adsorbed atoms, $l$ — the diffusion length, $D$ — the diffusion coefficient, $n_0$ — the concentration of adsorbed atoms and $\tau_0$ is the mean residence time of adatoms on tungsten [2,3,4,5].

To investigate the diffusion, the so-called "normalized mean square" of the ion current fluctuations was applied:

$$m = \langle di^2 \rangle T^2 / i^2 \tau_0 \approx D_0 \exp(-E/kT), \tag{2}$$

Table 1. The surface diffusion energies for alkali elements (E: activation energy for surface diffusion [eV], $r_i$: ionic radius of the adatom [Å])

| Adatom | $r_i$[Å] | E [eV] on W |
|---|---|---|
| Li | 0.60 | 0.67±0.10 |
| Na | 0.95 | 0.57±0.05 |
| K | 1.33 | 0.41±0.02 |
| Rb | 1.48 | 0.44±0.05 |
| Cs | 1.69 | 0.29±0.05 |

where $E$ is the activation energy for surface diffusion [2].

Value $\tau_0$ was estimated using the autocorrelation technique [2,3,9].

## EXPERIMENTAL

The measurements were performed in a stainless steel vacuum chamber allowing a high vacuum of $10^{-9}$ Torr. The procedure of depositing atoms on the emitter was described earlier [3,4] by the author, and details concerning the ion source construction can be also found there.

The anode of the thermal emission of ion source was a tungsten ribbon of size 10 × 0.8 × 0.025 mm.

The ion current fluctuations were amplified by a wide-band electrometer. The spectral density functions were investigated with a Unipan-237 selective nanovoltmeter with relative selectivity of $\Delta f/f = 0.014$.

## RESULTS AND DISCUSSION

The spectral density function can be approximated by the Lorentzian function:

$$S = S_0/[1 + (\omega\tau_0)^2], \tag{3}$$

where $\tau_0$ is the mean residence time of the adatoms on tungsten surface and $\omega = 2\pi f$.

It is well-known that the relationship between the $\langle di^2\rangle$ and the spectral density function is given by:

$$\langle di^2\rangle = \int_0^\infty S(f)df,$$

and

$$\langle di^2\rangle = \int_0^\infty S_0/[1 = (\omega\tau_0)^2]df = S_0/4\tau_0.$$

The low frequency spectrum is flat for $f\langle 1/2\pi\tau_0$. For $f \to 0$, $S \to S_0$ and its asymptotic value is:

$$S_0 = (2i_0\epsilon\mu/\xi_0 kTl)^2 n_0 D\tau_0^2.$$

The turnover frequency ($3dB$) $f_0 = 1/2\pi\tau_0$ and the high frequency asymptote is proportional to $f^{-2}$.

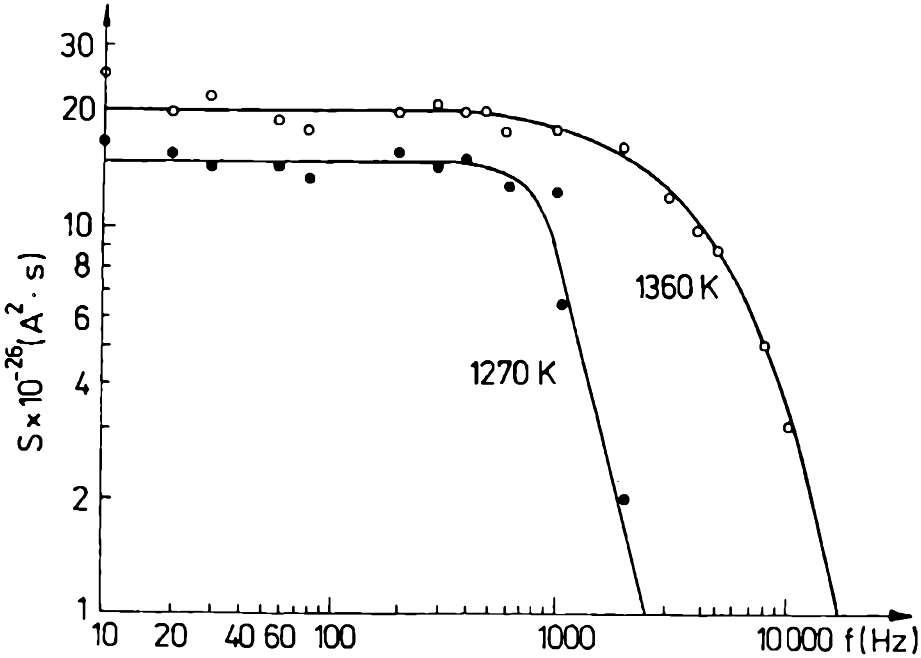

Fig. 1. Spectral density function $S(f)$ for potassium on tungsten for temperatures 1270 K and 1360 K

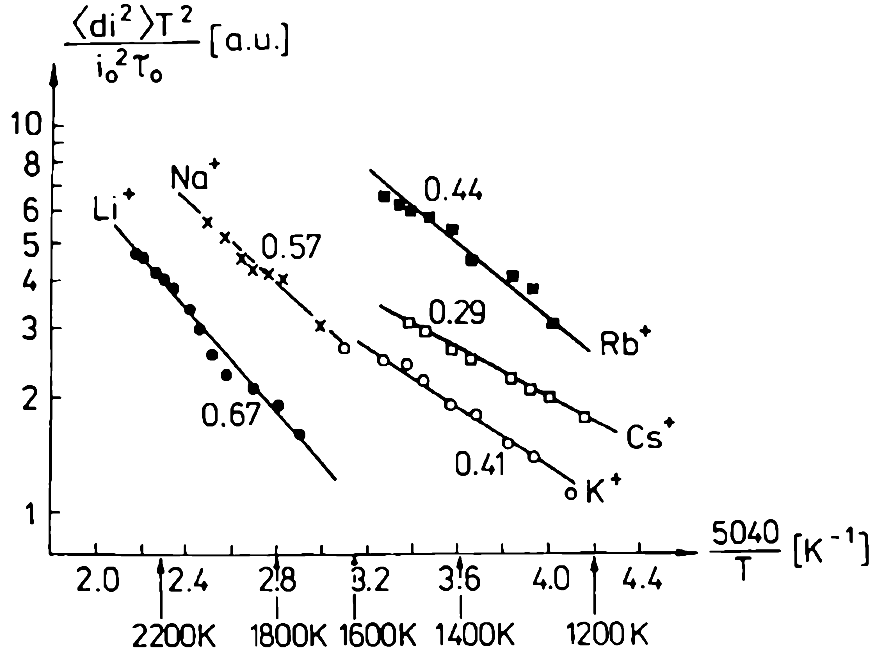

Fig. 2. Normalized mean square fluctuation as a function of the reciprocal temperature

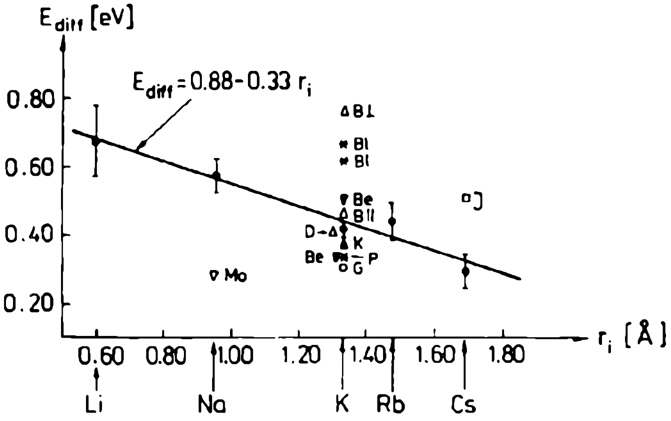

Fig. 3. Surface diffusion energy of alkali atoms on polycrystalline tungsten as a function of ionic radius $r_i$. (Mo - Morin [7], G - Gomer [10], Be - Bęben [11], P - Popp [12], K - Kleint [13], D - Dąbrowski [14], B - Bayat [15], Bl - Błaszczyszyn [16], J - Jamba [17])

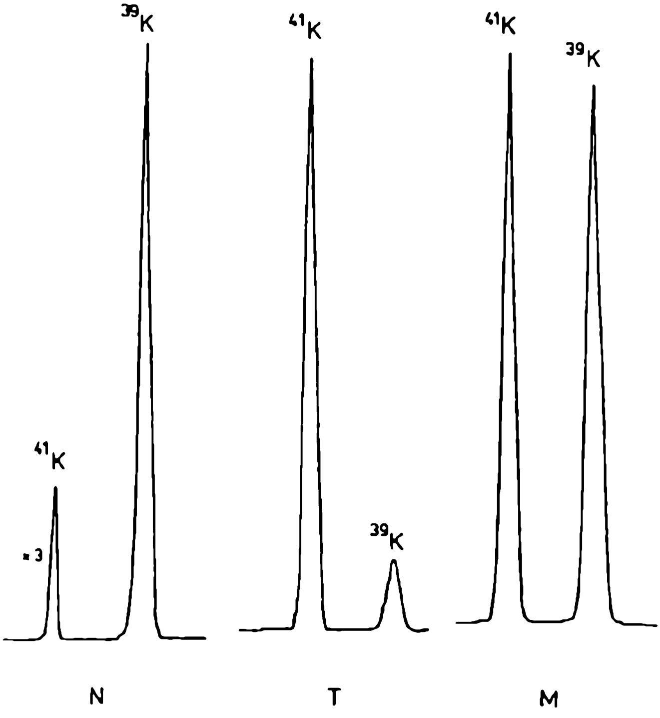

Fig. 4a. Mass spectra of the potassium (DC components): "N" — natural sample, "T" — tracer, "M" — mixture

The surface diffusion energies were determined from the thermal dependences of normalized mean square fluctuations $m$ (see Fig. 2).

It was determined that the values $E$ versus $r_i$ (ionic radius) represent a straight line (Fig. 3):

$$E = 0.88 - 0.33r_i.$$

In Fig. 3 the data obtained in these experiments are marked with full circles. For the sake of comparison some values of $E$, obtained by other authors are also included.

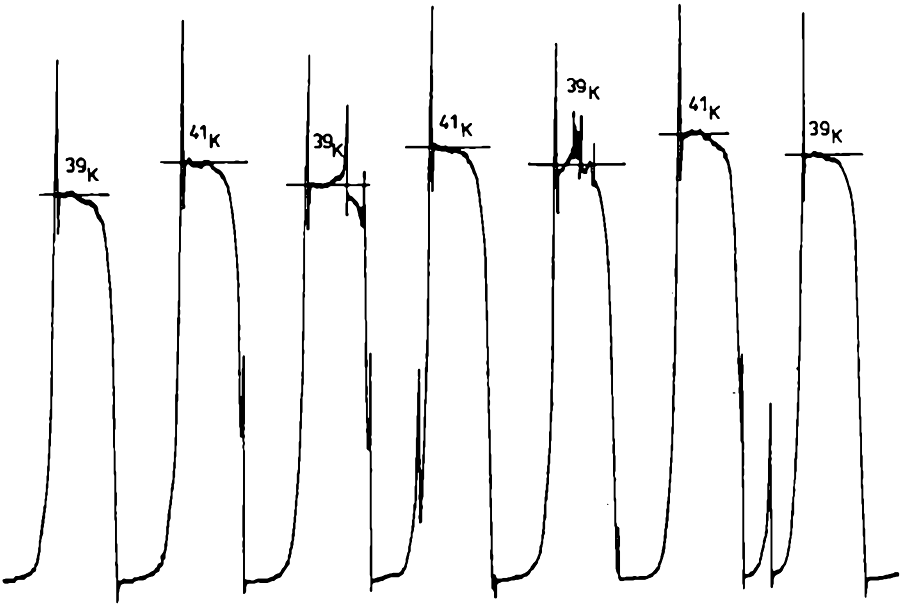

Fig. 4b. Mass spectra of the potassium obtained for noise components (sample "M")

The crystallographic structure of the tungsten ribbon was examined using the X-ray diffraction technique. From those one can see that (001) planes dominate, it means the polycrystalline ribbon reveals a (001) texture.

From the diffraction spectrum we can estimate the percentage contribution of various planes. The spectrum was compared with data for a powder sample.

An additional isotope fractionation effect was also reflected in the noise measurements. The isotopic ratio for potassium and lithium could be determined in these experiments by the analysis of noise components corresponding to the isotopes [3]. Measurements were performed on a magnetic mass spectrometer with 90° deflection and resolution of 300.

A mixture of two potassium samples: one of them was a normal isotopic composition ($^{39}$K: 92.96%, $^{41}$K: 7.03%), the other was a potassium tracer ($^{39}$K: 4.2%, $^{41}$K: 95.8%) was used in isotopic fractionation measurement. The mixture was prepared by isotope dilution technique [5,6].

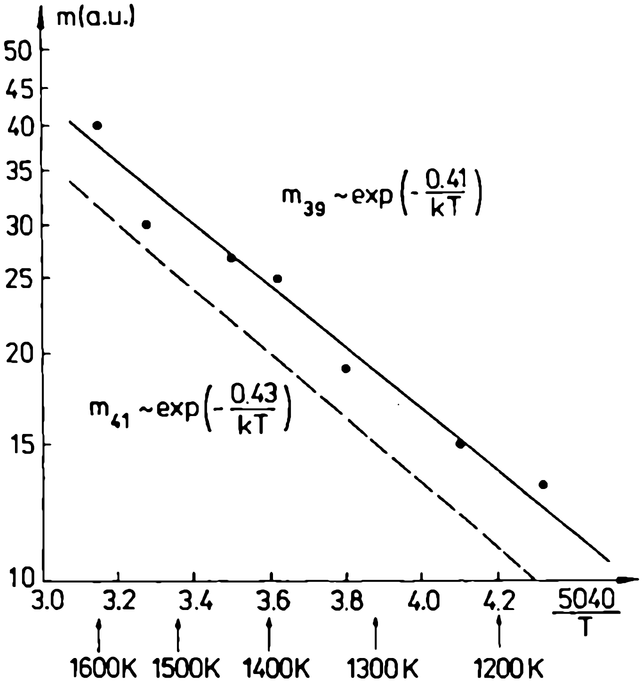

Fig. 5. Temperature dependence of the normalized mean square $m$ experimentally obtained for $^{39}$K (solid line) and calculated for $^{41}$K (dashed line)

The following isotopic composition was obtained for mixture: ($^{39}$K: 47.64%, $^{41}$K: 52.36%).

For two isotopes of potassium in sample M, the isotopic ratio $r_0$ obtained by measurement of DC ion current component: $r_0 = i^0_{41}/i^0_{39} = 1.072$ whereas the isotopic ratio $r_n$, obtained by measurement of noise component (cf. eg. (1)):

$$r_n - (\langle di^2_{41}\rangle / \langle di^2_{39}\rangle)^{1/2} = r_0\sqrt{D_{41}/D_{39} \cdot \tau^0_{41}/\tau^0_{39}},$$

$r_n = 1.05$.

Since $\tau^0_{41}/\tau^0_{39} = \alpha$ [7,8] and $\alpha = \sqrt{M_{41}/M_{39}}$, ($M_{39}$, $M_{41}$ are a mass of the isotopes; for potassium: $\alpha = \sqrt{41/39} = 1.025$, thus:

$$D_{39}/D_{41} = (r_0/r_n)^2 \cdot \alpha.$$

Let $\alpha = r_0/r_n$, this value will be called the "additional fractionation factor", therefore:

$$D_{39}/D_{41} = \alpha \cdot \alpha_1^2.$$

For investigated potassium sample $\alpha_1 = 1.02$ then $D_{39}/D_{41} = 1.07$ for $T = 1640$ K.

These results signified that for two potassium isotopes we observed two values of the surface diffusion energy:

$$D_{39}/D_{41} = [a_{39}\exp(-E_{39}/kT)]/[a_{41}\exp(-E_{41}/kT)] = \alpha \cdot \exp[(E_{41} - E_{39})/kT].$$

Our measurement give: $E_{39} = 0.41$ eV, therefore $E_{41} = 0.43$ eV.

Similar measurements and calculations performed for natural Li samples give: $r_0 = i_7^0/i_6^0 = 11.42 \pm 0.08$, $r_n = (\langle di_7^2\rangle/\langle di_6^2\rangle)^{1/2} = 9.5 \pm 0.2$ and $D_6/D_7 = 1.5$ (for $T = 2040$ K), therefore: $E_7 = 0.67 \pm 0.10$ eV [1] and $E_6 = 0.61 \pm 0.10$ eV.

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