TEMPERATURE DEPENDENCE OF THE NOISE SPECTRAL DENSITY FUNCTIONS OF POTASSIUM ADSORBED ON TUNGSTEN (112) PLANES*

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The temperature dependence of the field emission flicker noise of potassium adsorbed on W (112) was studied in sealed-off tubes with a fast spectrometer. Spectral densities $W(f_j)$ and exponents ε of the spectral density function $W(f) \sim f^{-\varepsilon}$ are presented for different coverages. A characteristic descent of $\varepsilon(T)$ with rising temperature is thought to be an indication of an order-disorder transition of the adsorbate.

1. Introduction

Adsorption of alkali metals on transition metals has attained widespread attention both from practical and theoretical aspects [1]. Potassium on tungsten proved to be a convenient system for studies with single crystal planes and much information has been obtained from FEM [2] and LEED measurements. At room temperature and higher temperatures surface diffusion plays an important role because its activation energy is some tenths of an electronvolt. Due to the influence of surface structure and the electronic properties of the adsorbate-substrate system there is a broad variety of possible diffusion

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mechanisms and not much is known in detail on surface diffusion especially for non-single atom coverages [3].

Apart from the well-known surface diffusion measurements by thermal activation after inhomogeneous deposition [4] field-emission flicker noise observations brought some interesting results on the dynamical processes of adsorbates [5, 6]. Noise power and spectral density functions are very sensitive to the stochastic properties of moving adparticles, and therefore it seemed worthwhile to study the temperature dependence of the spectral density functions $W(f)$ for potassium on tungsten. Because of the strong influence of coverage and substrate structure to be expected from former measurements [7] only the tungsten (112) plane was investigated.

2. Experimental

The experiments were carried out with all-glass sealed-off field emission tubes equipped with potassium source, Bayard-Alpert gauge and ion getter pump. By means of the ion pump PTJ 4 PIE Warsaw a vacuum of about 10^{-10} Torr was obtained. The field emission pattern could be observed on a fluorescent screen. An external magnetic deflection field served to adjust the investigated plane onto the probe hole in the screen where the emitted current could be detected by a Faraday collector with guard ring against secondaries. The potassium had been seven-fold destilled and was evaporated onto the tip from a glass ampule by means of a thermostat or from an electrically heated metal sheet. The emitter temperature was kept constant by a stabilized current through the emitter loop.

The noise measurements were done by a preamplifier with a d. c. path for controlling the magnitude and constancy of the collector current and an a. c. path leading after further amplification (amplifier M 60) to the frequency spectrometer FSP 80 (VEB Messelektronik Berlin). This spectrometer has 38 active filters with central frequencies between 2 Hz and 20 kHz. The noise voltage output of the filters is sequentially probed with a frequency of 25 Hz and analogue-displayed on a small TV screen. For every temperature three to six pictures of the screen each containing up to 8 different displays were recorded photographically. The spectral densities $W(f_i)$, $i = 1 \ldots 38$, were determined from optical projections of the negatives after dividing the amplitudes by the noise band width of every filter and eventually subtracting the amplifier noise. A least squares computer program served to calculate the exponents ε, their errors and the spectral densities $(W(f_j)$, $f_j \cong 0.1$, 1.0 and 10 kHz. Visual inspection of the double-logarithmically plotted $W(f_i)$ values was used to decide on eventually choosing different slopes, i. e. exponents and the knee frequencies between different slopes. As was pointed out already [7] the error bars $(2\Delta\varepsilon)$ in the figures are fitting errors of the least squares method while the true errors may be greater. The high speed of these noise measurements as compared to the former point by point recording [7, 8] allowed slighter restrictions to be made on the long time constancy of the tip state, but has the disadvantage of somewhat higher errors of the slope especially at lower frequencies. (Occasionally some ambiguity could arise as to choose one or two slopes for one spectral density function. To get a first survey on the temperature dependence of the slopes these questions were left for more detailed measurements to follow.)

3. Results

Fig. 1 and Fig. 2 show the spectral densities $W(f_j)$ and the slopes $\varepsilon(f_j)$ of the spectral density functions $W(f)$ for a potassium coverage of $\bar{\theta} = 0.3$ on $W(112)$. The coverage scale is the same as in the paper of Schmidt and Gomer [9] where the work function mini-
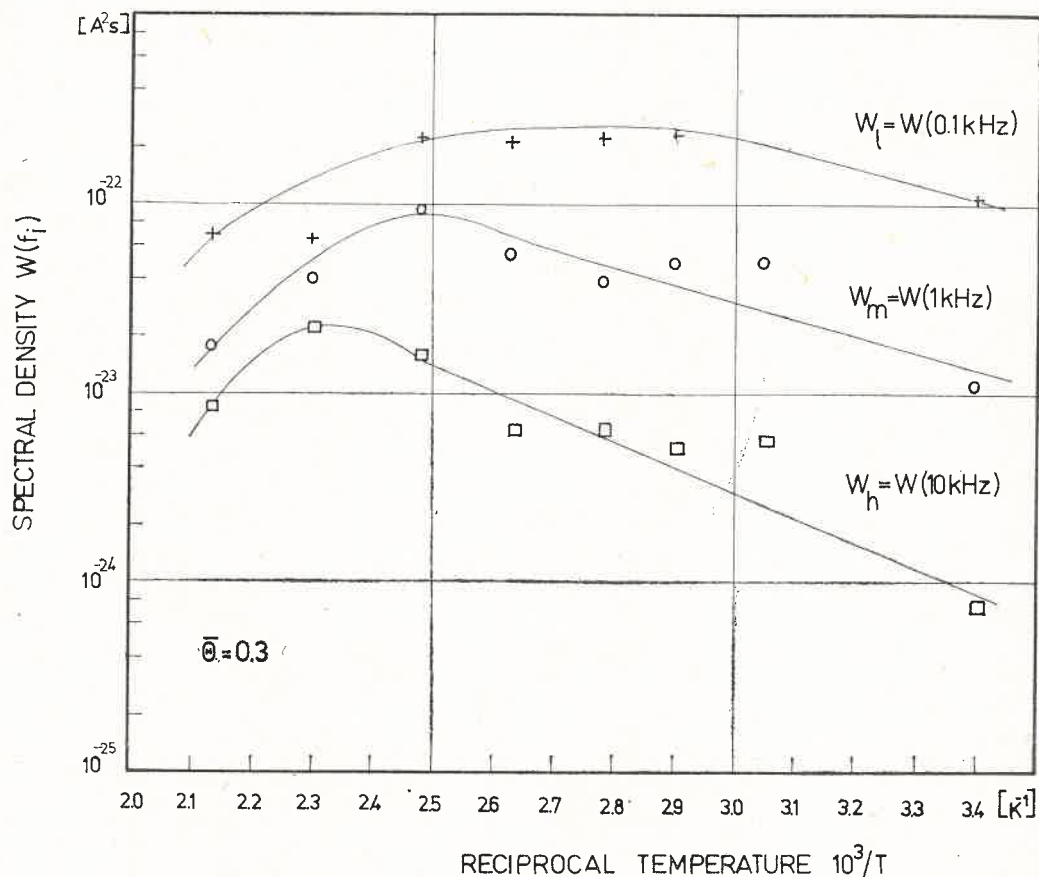

Fig. 1. Temperature dependence of the spectral densities at different frequencies, potassium coverage $\bar{\theta} = 0.3$

mum of the total tip corresponds to $\bar{\theta} = 0.83$. Typical spectral density functions for K on $W(112)$ were already presented in Ref. [7] (Figs 5, 6 and 7), therefore Fig. 1 shows only the spectral density values for a lower, medium and higher frequency (0.1, 1.0 and 10 kHz, resp.) plotted versus $10^3/T$. With increasing temperature $W(f_j)$, the noise power per frequency interval of 1 Hz, generally also increases but the data scatter somewhat indicating eventually a lack of constancy of the coverage. Fig. 2 represents a plot of the exponents ε_j of the spectral density function
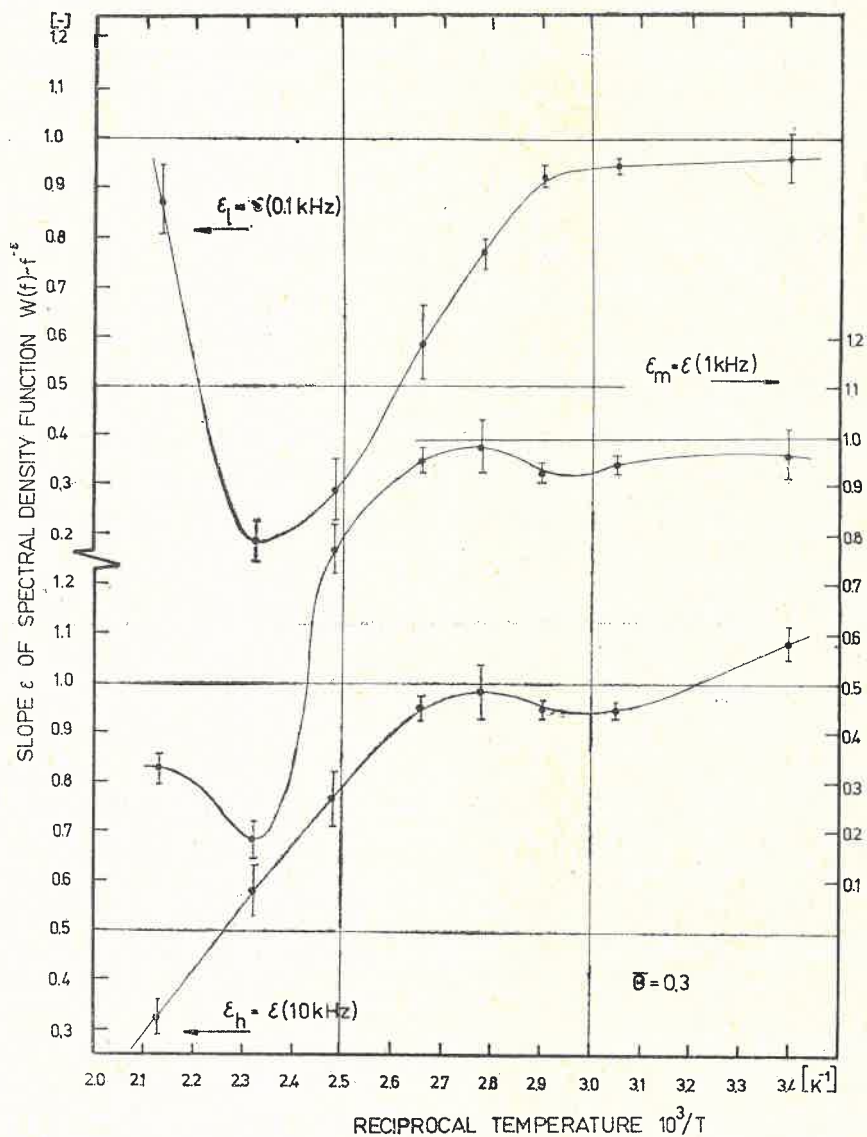
$$W(f) \sim f^{-\varepsilon} \tag{1}$$

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Fig. 2. Temperature dependence of the slopes of the spectral density functions at different frequencies, potassium coverage $\bar{\theta} = 0.3$

at the three frequencies l, m, h chosen. Especially at 100 Hz the slope decreases continuously with increasing temperature to very small values below 0.2. Finally, at the highest temperatures just before the begining of desorption, the slope increases, marking a minimum ε_l and ε_m at about 425 K. Fig. 3 gives the noise for a coverage of $\bar{\theta} \approx 0.55-0.60$. The spectral densities show an increasing noise power with rising temperature and for lowest frequency a slight indication of a maximum of $W(f_l)$ is again present. Unfortunately the number of experimental points is small. This causes an uncertainty which is expressed
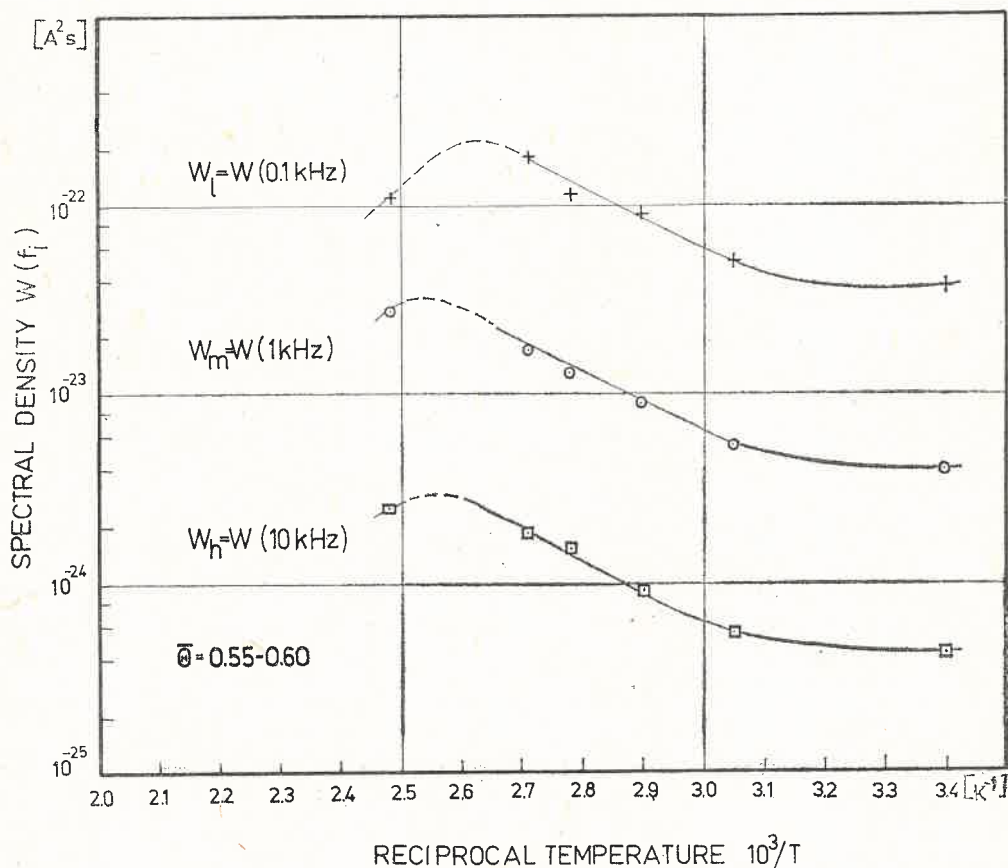

Fig. 3. Temperature dependence of the spectral densities at different frequencies, potassium coverage $\bar{\theta} = 0.55-0.60$

by the dashed lines in Fig. 3, drawn somewhat arbitrary. The existance of the maxima for the frequencies 1 kHz and 10 kHz is therefore questionable and is only justified by extrapolation from the other measurements. The slopes ε_j (Fig. 4) have the marked descent only for the small frequencies range while the medium and high frequencies slopes are nearly constant.
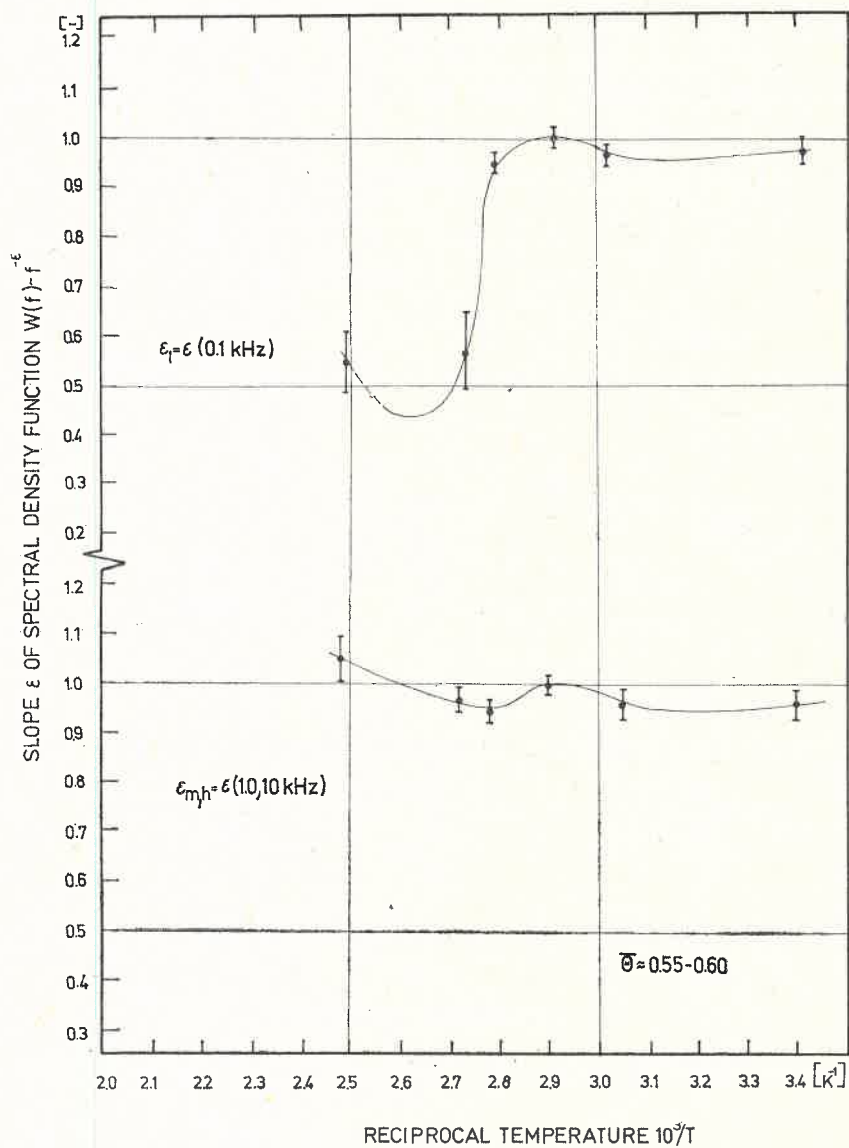
Fig. 4. Temperature dependence of the slopes of the spectral density functions at different frequencies, potassium coverage $\bar{\theta} = 0.55-0.60$. (The slopes for 1.0 kHz and 10 kHz are equal.)

With increasing coverage the maxima of $W(f_j)$ are even more pronounced as can be seen in Fig. 5 for $\bar{\theta} = 0.65$. Here another tendency of the spectral densities is obvious to show their maximum at higher temperatures for higher frequencies. The accompanying slopes ε (Fig. 6) present nicely the rather steep descent with temperature and a slight minimum to follow. Here all spectral density functions have only a single slope in the frequency range investigated. Finally, for the coverage $\theta = 1$ the features of the spectral
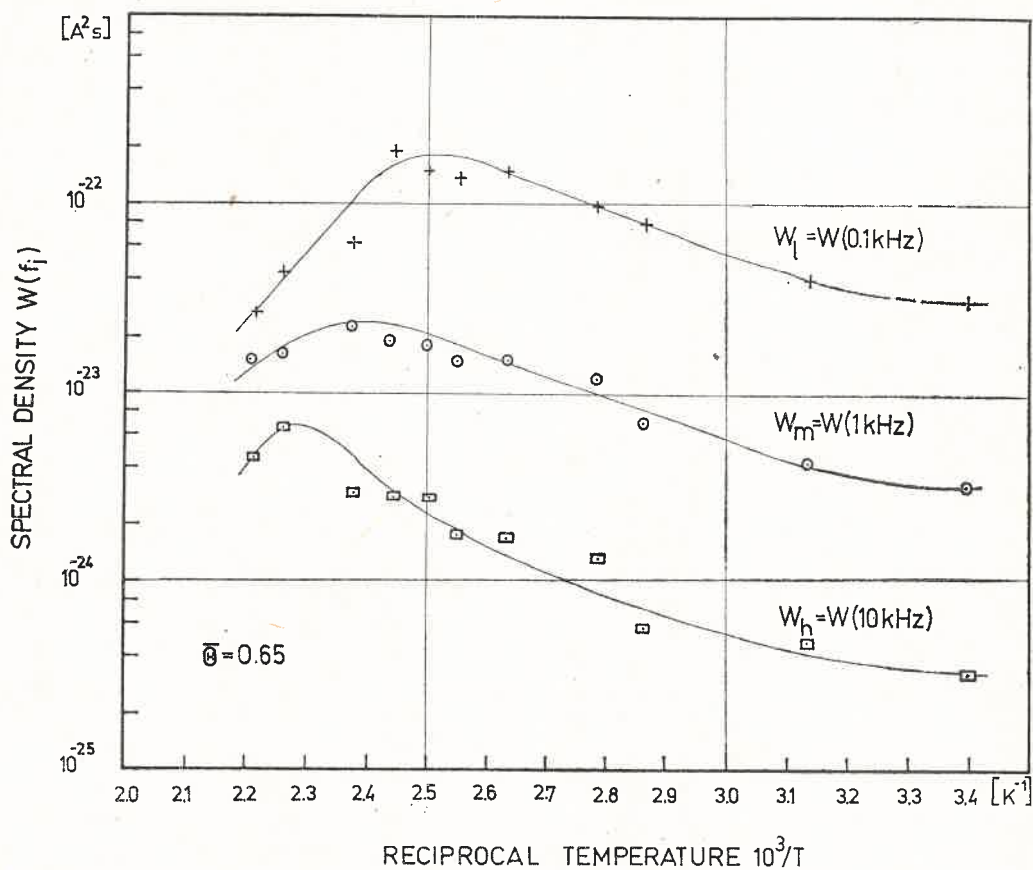
Fig. 5. Temperature dependence of the spectral densities at different frequencies, potassium coverage $\bar{\theta} = 0.65$

densities discussed above are again present (Fig. 7). A relatively weak decrease of $\varepsilon(T)$ with rising temperature can be observed in Fig. 8 for higher temperatures. The low temperature part of the curves has a different character.

4. Discussion

Increasing noise power with increasing temperature is often observed and simply understood as due to enhanced diffusion. "Noise activation energies" [5] may be evaluated from the $W(f_j)$ plots below the maxima. More difficult to interpret are the maxima

of $W(f_j)$ vs. $10^3/T$, which are not due to evaporation of potassium as may be thought at a first glance. (Another possibility would be a reversibly decrasing K-population on the plane under investigation. As a consequence a higher concentration on other planes or on the shank of the emitter should result which is not much plausible). While other noise models fail to describe such behaviour, the surface diffusion model [10] includes the possibility of spectral density maxima. This was already pointed out by Fig. 5 of Ref. [10] and found also with other adsorption systems [11]. In this model the relative occupation
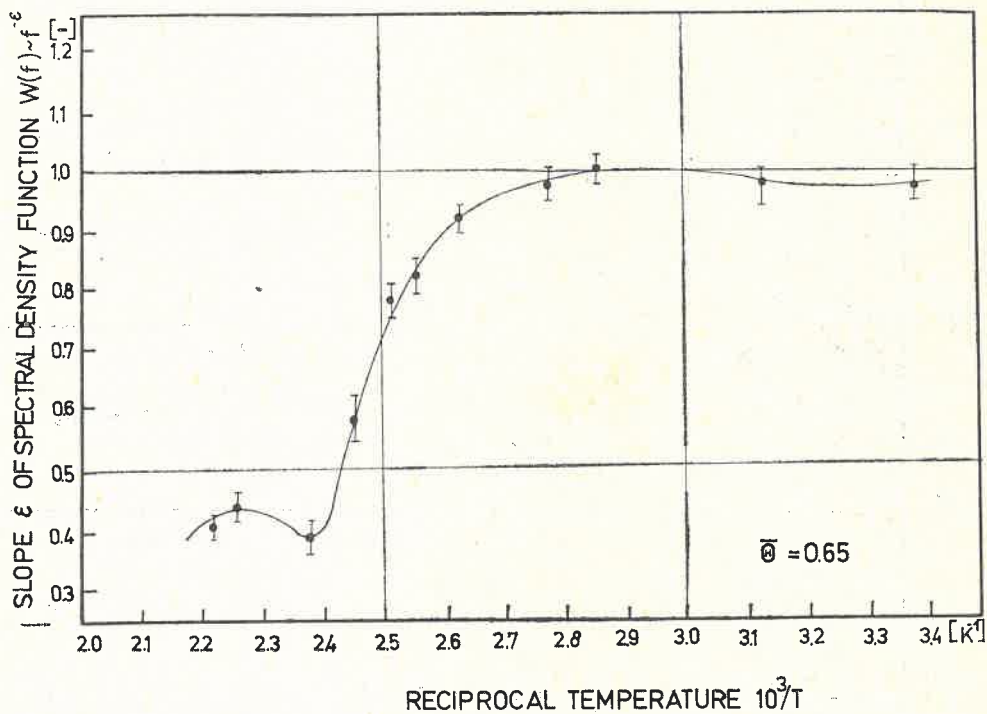

Fig. 6. Temperature dependence of the slope of the spectral density functions, potassium coverage $\bar{\theta} = 0.65$
(The slopes for all frequencies investigated are equal).

of the stronger binding sites decreases with rising temperature in favour of the weaker binding sites and the transition rate K between stronger and weaker binding sites may go through a maximum. Also the temperature independent spectral densities at high coverage as observed up to $10^3/T = 2.9$ for $\bar{\theta} \approx 1$ (Fig. 7) can be obtained with the surface diffusion model (Eq. (14) of Ref. [10]).

While the temperature dependence of the spectral densities was observed already [5] though in a somewhat integrated form,

$$\overline{\delta I^2_{f_1 \ldots f_u}}(T) = \int\limits_{f_l}^{f_u} W(f)df, \tag{2}$$

no slope versus temperature curves are available. The main result of the above measurements is the strong fall or descent of ε with rising temperature and an eventually following minimum. The patch model of Timm and Van der Ziel [12] reveals no variation of the slope with temperature in the low or high frequency limit of the spectrum. For a similar model of Gomer [13] also with adatom concentration fluctuations in the probed area no
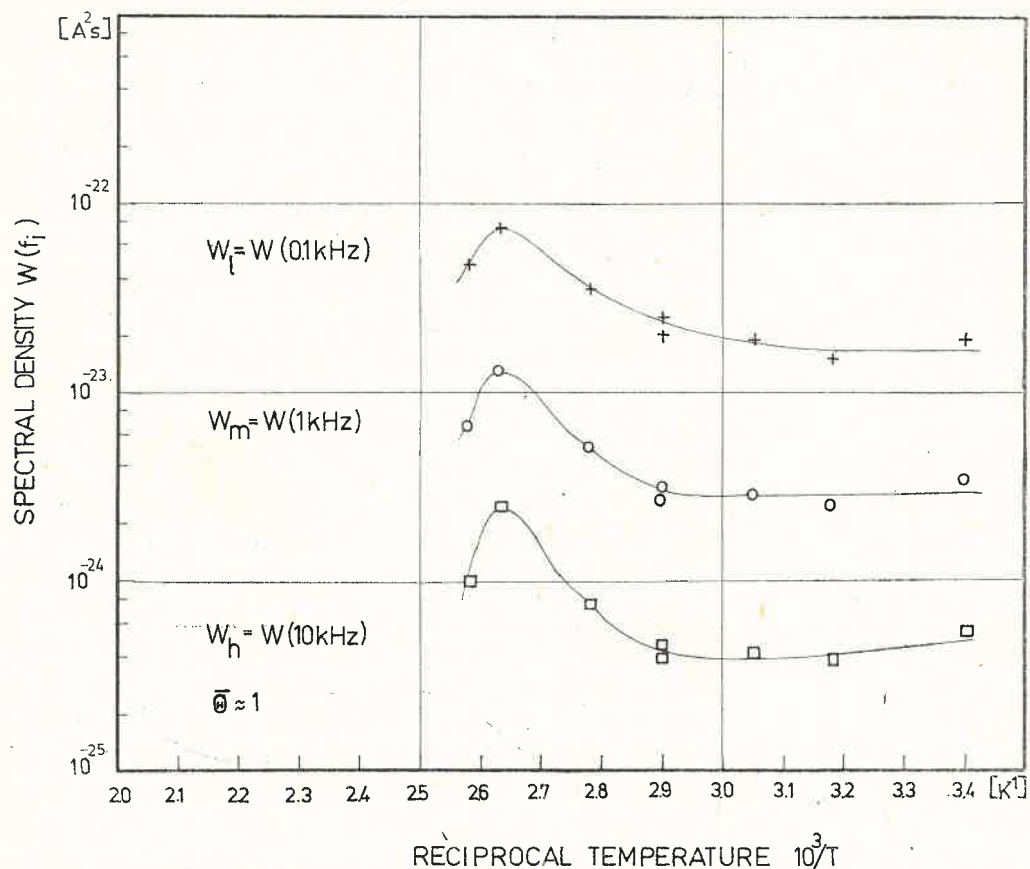

Fig. 7. Temperature dependence of the spectral densities at different frequencies, potassium coverage $\overline{\theta} = 1$

spectral density functions were given. The surface diffusion model, however, allows for a temperature dependence of the slopes, but does not give the ε descent as described above. Here the slope is

$$\varepsilon = 2 - \frac{\lambda_c v}{4\pi D}, \tag{3}$$

and depends on the capture diameter λ_c, a diffusion velocity v and the diffusion coefficient D. Using the diffusion velocity for localized adatom diffusion [14],

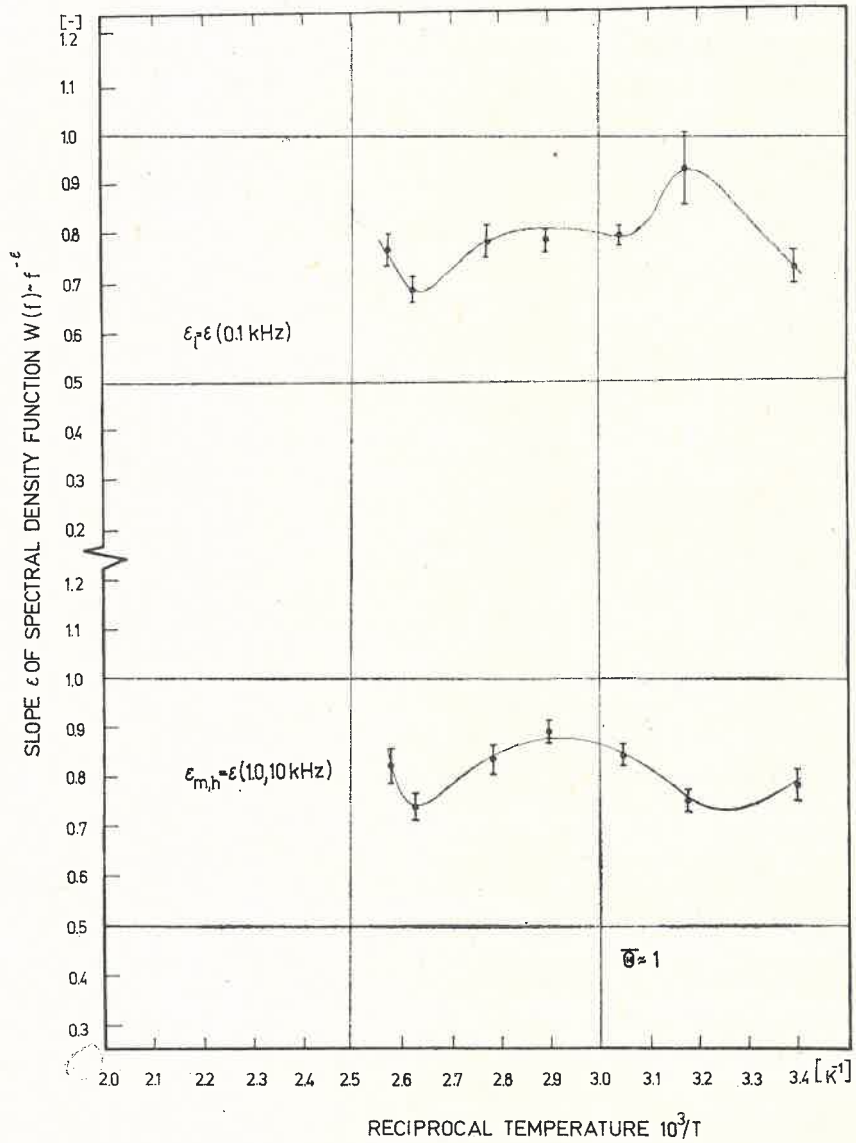$$v = \left(\frac{kT}{2\pi m}\right)^{1/2} \tag{4}$$

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Fig. 8. Temperature dependence of the slopes of the spectral density functions at different frequencies. potassium coverage $\bar{\theta} = 1$. (The slopes for 1.0 kHz and 10 kHz are equal.)

and the diffusion coefficient:

$$D = D_0 \exp\left[-\Delta Q/kT\right],\tag{5}$$

the slope varies as

$$\varepsilon = 2 - \frac{\lambda_c}{(2\pi m)^{1/2}} \frac{(kT)^{1/2}}{D_0 \exp\left[-\Delta Q/kT\right]} .\tag{6}$$

Because the exponential function dominates, ε should increase with temperature contrary to the experiments.

Therefore, another mechanism should be considered. In the case of the strong adatom-adatom repulsion — existing apart from the adsorbate-substrate interaction — the formation of two-dimensional adsorbate lattices was observed by many authors. Such 2D lattices were investigated mainly by means of low energy electron diffraction (LEED). Gerlach and Rhodin [15] found that the strong repulsive forces between alkali adatoms on the nickel (111) and (100) planes led to adlayers with uniformly spaced adatoms. Similar investigations for tungsten substrates were carried out by the Kiev group. Medvedev et al. [16] studied the structure of adsorbed sodium on the $W(011)$ plane in a broad range concentration and temperature. Voronin et al. [17] observed a $c(2 \times 2)$ cesium structure on the $W(100)$ plane. Kanash et al. [18] investigated ordered structures of strontium on tungsten; Medvedev and Jakivtshuk [19] found a potassium $c(2 \times 2)$ structure on $W(112)$ corresponding to the work function minimum. Many investigators [15, 18–21] observed phase transitions in alkali and rare earths adlayers mainly with increasing coverage. Order-disorder transitions were found not only for alkali layers but also for gas adsorption [22]. Ertl and coworkers [23] developed Monte Carlo and analytical treatments of these order-disorder transitions (using in the latter case a 2D-Ising model). In the above mentioned flicker noise models [10, 12, 13] no ordered adlayer structures nor any phase transitions were assumed. In particular, consequently, no difference of the noise for coherent and incoherent structures has been considered. In alkali adlayers, where usualy the adparticles are uniformly spaced, coherent structures appear with increasing adsorbate concentration only for distinct coverages. The flicker noise then should stem from single adparticles leaving their site in the adsorbate structure by thermal excitation and going back to this place or another. This explanation was already considered by Męclewski [24], but an evaluation of the spectral density function has not been done. Because an activation energy is necessary for leaving the adsorbate lattice site, a formal similarity to the surface diffusion model can be expected giving the qualitative features of the spectral densities. With increasing temperature the adsorbate lattice undergoes a phase transition from an ordered to a random configuration. While in LEED experiments the intensity of the extra spots can be used as an order-disorder parameter the exponent ε of the noise spectral density functions appears to be a somewhat similar parameter. $\varepsilon(T)$ contains additional information if there are different ε in different frequency ranges. On the (112) tungsten plane should exist two different activation energies for single adatom diffusion in the $[11\bar{1}]$ and $[\bar{1}10]$ direction. This assumption is based on the consideration of the substrate structure of the (112) plane which can be found for instance in Fig. 3 of reference

[19] or Fig. 2 of reference [25]. Experimental results which are in favour of this assumption were obtained by Drechsler [26]. He observed W surface self-diffusion and Ba diffusion on tungsten in the prefered direction $[11\bar{1}]$ ("gerichtete Oberflachendiffusion"). Different activation energies should show up in different exponents of $W(f)$ as observed especially on $W(112)$.

Though this explanation is only qualitative a more extended investigation now under way should give a better insight in the complicated stochastic properties of adsorbed atoms with high mutual interaction and allow to check the hypothesis of $\varepsilon(T)$ to act as order--disorder parameter as stated above.

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