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**Determination of activation energies of mass transport processes on  
Ag(111)-electrodes in aqueous electrolyte**

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**Abstract**

Using temperature variable STM studies of step fluctuations on Ag(111)-electrodes in electrolyte, we have measured the activation energies for the dominant atomic mass transport processes close to the dissolution potential of Ag into the electrolyte. The results are in agreement with previous potential dependent studies [Surf. Sci. 384 (1997) 168] at room temperature. Temperature dependent studies of step fluctuations are not restricted to the Ag electrode and the electrolyte chosen in the presented experiments, but are generally applicable to electrodes in liquid environment. They are the only studies available so far to determine activation energies of atomic processes at the solid/liquid interface.

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## 1. Introduction

The kinetics of chemical reactions on metal electrodes is considerably affected by surface defects. The specific adsorption of anions on surfaces, the dissolution of metal electrodes as well as metal deposition from the electrolyte onto the electrode preferably start at defects. In particular, steps and kinks may act as reactive sites for electrochemical processes. Steps and kinks are no static objects but are mobile on the time scale of atomic diffusion processes [1-5]. Kinks move along steps by detachment of kink atoms to the step edge or onto the surface. The motion of adatoms and kinks along steps gives rise to fluctuations of the steps around their mean position. These step fluctuations depend on temperature and may be strongly influenced by the electrochemical potential of the electrode in electrochemical environment [1-3, 6]. Furthermore, the dynamics of steps and kinks may significantly change, if surfaces are covered with adsorbates [6]. Hence, detailed studies of step and kink dynamics under various experimental conditions are the basis to the understanding of chemical reactions on metal electrodes in electrolyte.

Since its invention, the scanning tunneling microscope (STM) [7] has proved to be a powerful tool to investigate surfaces and surface defects in UHV as well as in the electrochemical cell [8-10]. In contrast to classical electrochemical experiments, STM studies on metal electrodes consider local phenomena on the surface and are therefore, in particular, suitable to investigate the kinetics and dynamics of local surface defects. Although the STM does not provide snap-shot images of the surface due to the finite scan speed (as becomes obvious by the frizzy appearance of monatomic high steps [11-13] and island edges [14-16]), the analysis of mobile steps by specific theoretical models [17-20] analogue to the theoretical description of the decay of surface profiles [21] gives information on the dominant atomic mass transport diffusion processes causing step fluctuations. Quantitative studies on the step dynamics have been performed in UHV for about a decade now for various metal surfaces [12, 13, 22-32] as

well as for semiconductor surfaces [33, 34] (for an overview see also refs. [35] and [36], respectively). From these studies, the mass transport processes at steps were determined and temperature variable experiments yielded values for the activation energies [13, 23-25, 31].

The dynamics of steps can also be investigated on metal electrodes in electrolyte. Here, the analysis of step fluctuations is the only method to date to study atomic diffusion processes quantitatively. First experiments were performed on Ag(111) [2, 3], Cu(100) [3] and Au(111) [6] electrodes at room temperature. In these studies was demonstrated that activation energies of the dominant mass transport processes may, in principle, be determined by investigating the potential dependence of the step fluctuations (if there is any). When activation energies are determined from the potential dependence of the step dynamics, however, a theoretical ansatz must be used to relate the energies to the electrode potential. In the studies mentioned before, a linear relationship has been assumed to describe the potential dependence of the activation energies. Although this ansatz seems to be quite reasonable at least for not too large potential ranges as was recently demonstrated by Haftel and Einstein [37] in calculations using the surface-embedded-atom-model [38], it has so far not been confirmed experimentally whether the linear ansatz is justified. Furthermore, the determination of activation energies for mass transport processes on metal electrodes in liquid environment is applicable merely to those systems, where a strong potential dependence of the step dynamics is observed. This is not always the case as was recently demonstrated by our group for Cu(111) electrodes in chloric acid [39]. Therefore, temperature variable studies are desirable to obtain numbers for the activation energies of atomic mass transport on metal surfaces in electrolyte.

Here, we report for the first time of a temperature variable study of step fluctuations on an Ag(111) electrode in liquid environment. We determine the activation energy and the pre-exponential factor of Ag desorption into a copper-containing electrolyte and find that the

results are in excellent agreement with the previous, potential-dependent studies on Ag(111) at room temperature [2, 3].

## 2. Experimental

The experiments were performed with the electrochemical version of a Topometrix TMX 2010 Discoverer STM. The tip and sample potential was independently controlled by a bipotentiostat. The sample temperature was varied using a home-built heating- and cooling-stage based on a Peltier element under the electrochemical cell. Fig. 1 shows a schematic sketch of the microscope socket in tunneling configuration with the heating/cooling stage. The temperature is regulated by an analog control loop where the sample temperature is monitored by a thermocouple connected to the back side of the electrochemical cell. The temperature at the sample surface deviates slightly from the reference value due to thermal loss across the bottom of the electrochemical cell and the sample. The temperature  $T_S$  as measured at the surface of the sample is a linear function of the reference temperature as shown in Fig. 2.

$T_S$  was measured, when thermal equilibrium was reached at the sample. When the reference temperature  $T_0$  is changed by several degrees, thermal equilibrium at the sample surface is established within a few minutes. Then, the thermal drift of the microscope is smaller than 50 Å/min. The maximum and minimum temperatures that can be reached at the surface are limited by convection in the electrolyte causing a strong drift during the scanning process and by the freezing point of the electrolyte, respectively. The maximum temperature is furthermore restricted by the increased evaporation rate of the electrolyte at elevated temperatures. Hence, reliable experiments in aqueous electrolytes are available in a temperature range between 5 and 50°C.

The tunneling tips were etched in a cyanide solution from a Pt/Ir (80:20) wire and coated with an electrophoretic paint (BASF Glasophor) by means of galvanostatic deposition, leaving only the foremost part of the tunneling tip exposed to the electrolyte [40]. As an electrolyte, we

used 1mM CuSO<sub>4</sub> + 0.05M H<sub>2</sub>SO<sub>4</sub>, which was made from suprapure (H<sub>2</sub>SO<sub>4</sub>) and p.a. (CuSO<sub>4</sub>) chemicals (Merck) and Milli-Q water ( Millipore, 18.2 MΩcm<sup>-1</sup> ). Copper and platinum wires of high purity (Goodfellow, 99.999 %) served as a reference and counter electrode, respectively.

The measurements were performed between about 295 and 310K. With increasing sample temperature, the potential at the reference electrode shifts less than about 10mV towards smaller values. Since the shift in the potential is about the same order of magnitude as the potential drift typical for studies in STM cells with Pt reference electrodes, the potential was not corrected for this small error. The final results for the activation energies should nevertheless give about the right numbers. We note, however, that in measurements covering a larger temperature range, the potential shift at the reference electrode should be accounted for.

The experiments were performed on Ag(19,19,17) electrodes (with diameter 12 mm and thickness 2.5 mm), which are vicinal to the (111)-plane. The (19,19,17) surface is tilted by 2.9° into the  $[\bar{2}11]$ -direction. The electrodes were cut from a single crystal rod by spark erosion, oriented by diffractometry and electrochemically and mechanically polished to the desired angle within 0.1°. The geometrically ideal surface consists of 5nm wide (111)-terraces corresponding to 19.5 atomic rows. The terraces are separated by monatomic (111)-steps (B-steps) along the dense  $[01\bar{1}]$ -direction. On the real surface, however, the terrace width may deviate from the nominal width. This may be, first, due to the terrace width distribution [17, 41-44] and, second, due to occasionally observed step pinning. The latter may also give rise to steps oriented along low-symmetry directions. These steps have a high density of forced kinks. To avoid errors in the analysis of step fluctuations, merely surface regions free of step pinning were considered.

Prior to experiment, the Ag crystals were chemically polished in a  $\text{H}_2\text{O}_2$ /cyanide solution and subsequently flame-annealed while the surface was kept in a flowing argon atmosphere. The crystals were re-oriented and re-polished after approximately ten individual experiments.

We analyzed the step fluctuations on Ag(19,19,17) between 296 and 311K while the electrode potential was held constant at +50 mV vs. SCE in all studies, which is about 50mV below the onset of rapid Ag dissolution into the electrolyte. In all experiments, a tunneling current of 2 nA was used and the images were obtained in the constant-current mode with a tunneling bias of  $-60\text{mV}$ . We recently demonstrated that the step fluctuations are not affected by the tunneling tip, when these tunneling parameters are used [3].

For the analysis of step fluctuations we used so-called time images [45], where the tip scans repetitively across the same line. In these images, the vertical axis represents a time axis, whereas the horizontal axis is a spatial axis. The scan direction was chosen such that the spatial axis was oriented approximately perpendicular to the steps. Fig. 3 shows a time image of the stepped Ag(19,19,17) surface at 296 K.

### 3. Theory

Step fluctuations are analyzed by means of a time correlation function  $F(t)$ , which is defined as the mean square deviation in step positions at different times  $t$  and  $t_0$ :

$$F(t) = \left\langle \left( x(t) - x(t_0) \right)^2 \right\rangle. \quad (1)$$

Depending on the dominant mass transport mediating the step fluctuations,  $F(t)$  obeys a power law in the time  $t$  and in the mean step distance  $L$ , with exponents  $\alpha$  and  $\delta$ , respectively [18, 19]:

$$F(t) = C(T)(t - t_0)^\alpha L^\delta, \quad (2)$$

where the time and the step-step distance exponents  $\alpha$  and  $\delta$  may assume different values:  $\alpha=1/4$  and  $\delta=0$ , if edge diffusion is the dominant mass transport at the steps. No dependence on the step-step distance  $L$  is found also in the cases where atoms are exchanged with the terraces and terrace diffusion is either fast ( $\alpha=1/2$ ) or slow ( $\alpha=1/3$ ). If atoms are exchanged between steps and the electrolyte,  $\alpha=1/2$  and  $\delta=1/2$ . Further mass transport cases and the corresponding exponents are discussed in refs. [18, 19]. A presentation of the time laws adapted to the specific needs of an experimentalist is given in refs. [2, 35]. In eq. (2),  $C(T)$  is a temperature dependent pre-factor which contains all formation and activation energies related to the dominant mass transport at the steps. Details for the mass transport case relevant to the case of Ag(19,19,17) in electrolyte are presented below.

Previously, we have shown that the dominant mass transport process on stepped Ag(111) electrodes in sulfuric acid at room temperature depends on the electrode potential [2]: Below 0mV vs. SCE, edge diffusion is the dominant transport mechanism, i.e.,  $F(t) \propto t^{1/4}$ . For electrode potentials higher than 0mV vs. SCE, mass is exchanged between the electrode surface and the electrolyte, i.e.,  $F(t) \propto t^{1/2}L^{1/2}$ . The temperature variable studies presented here were performed at +50 mV vs. SCE, and hence, the step fluctuations are due to atomic exchange between the Ag steps and the electrolyte. It is noted that no net flux of Ag atoms into the electrolyte is apparent, which is confirmed by the fact that the mean step edge positions are stable during the experiment. The time correlation function  $F(t)$  for the particular mass transport situation is given by [2]

$$F(t) = (P_k c_s v_{sl})^{1/2} t^{1/2} L^{1/2}. \quad (3)$$

The equilibrium adatom concentration  $c_s$  on the surface is given by

$$c_s = e^{-\frac{E_{ad}}{k_B T}}, \quad (4)$$

where  $E_{ad}$  is the formation energy of an adatom from a kink onto the terrace.

$v_{sl}$  is the evaporation rate from the surface into the electrolyte and is given by

$$v_{sl} = v_0 e^{-\frac{E^\ddagger}{k_B T}}. \quad (5)$$

Here,  $E^\ddagger$  is the potential-dependent activation barrier for Ag dissolution into the double-layer of the electrolyte and  $v_0$  is the pre-exponential factor.

The kink concentration  $P_k$  can be expressed in terms of the kink energy  $\varepsilon$  [41]:

$$P_k \approx 2 e^{-\frac{\varepsilon}{k_B T}}. \quad (6)$$

Eq. (6) holds for low temperatures, i.e.,  $\varepsilon \gg k_B T$ . Inserting eqs. (4)-(6) into eq. (3) one obtains:

$$F(t) = \sqrt{2v_0} e^{-\frac{\varepsilon + E_{ad} + E^\ddagger}{2k_B T}} L^{1/2} t^{1/2}. \quad (7)$$



Note that in eq. (7) all quantities are given in atomic units, i.e.,  $F(t)$  and  $L$  are given in units of  $a_{\perp}^2$  and  $a_{\perp}$ , respectively, where  $a_{\perp}$  is the distance between dense atomic rows on the (111) surface.

While the time correlation function as given in eq. (7) vanishes for  $t=0$ , we showed that  $F(t)$  as measured for Ag(111) in sulfuric acid has a constant contribution at  $t=0$  [2], i.e.,  $F(t)$  has the form

$$F(t) = F(0) + \sqrt{2\nu_0} e^{-\frac{\varepsilon + E_{ad} + E^{\ddagger}}{2k_B T}} L^{1/2} t^{1/2}. \quad (8)$$

The physical origin of the constant offset  $F(0)$  is not explained yet. Previously, we proposed that  $F(0)$  arises from tip-surface interactions [2]. More recent STM investigations show, however, that  $F(0)$  is independent of the tunneling resistance for moderate tunneling parameters [3]. The constant offset may also arise from rapid back and forth hopping of kinks at the steps, which saturates within the time needed for one scan line. In this case, the constant offset should be temperature dependent.

#### 4. Experimental results

We first consider the temperature dependence of the constant offset  $F(0)$  as shown in Fig. 4. Despite some scattering,  $F(0)$  appears to be independent of temperature. The average value of  $F(0)$  is  $2.5 \pm 0.9$  ( $a_{\perp}^2$ ) in accordance to our previous study, where we showed that  $F(0)$  is independent of the electrode potential and of the order of 2.1 [2]. To analyze the pure time dependence of  $F(t)$  we have therefore corrected the experimental data for the constant contribution at  $t=0$  in the following.

Fig. 5 shows the time correlation function  $F(t)$  for three different temperatures measured in a surface areas with mean step distance of  $L=70\text{\AA}$ , corresponding to  $L=28a_{\perp}$ . The step

fluctuations increase with increasing temperature and so does  $F(t)$ . The solid lines in Fig. 5 are least square fits to eq. (7) with constant exponents  $\alpha=\delta=1/2$ , and the temperature dependent pre-factor  $C(T)$  being the fit parameter. From such fits we find that  $F(t)$  obeys a  $L^{1/2}t^{1/2}$ -law between  $T= 296$  and  $311\text{K}$ .

The activation energy for the mass transport is determined from the temperature dependence of the value of  $F(t)$  at a distinct time  $t_0$ . Fig. 6 shows an Arrhenius-plot of the correlation value  $F(t_0)$  at  $t_0=2\text{s}$ . Here, we have included data from areas with different step densities. In order to plot the data into the same view graph, we scaled the experimental data for  $F(2\text{s})$  by the square root of the step-step distance  $L$  (in units of  $a_{\perp}$ ). Then, the data points fall on a straight line and the activation energy is

$$E_t=0.55\pm 0.1\text{eV} \quad (9)$$

From the extrapolation of the data to  $T \rightarrow \infty$  one obtains the pre-exponential factor

$$v_0 = 3.4 \times 10^{16 \pm 3} \text{ s}^{-1}. \quad (10)$$

## 5. Discussion

According to eq. (7), the activation energy  $E_t$  can be expressed in terms of the kink energy  $\varepsilon$ , the desorption energy of Ag atoms in the electrolyte  $E^{\neq}$  and the adatom formation energy  $E_{\text{ad}}$  :

$$2E_t = E_{\text{ad}} + E^{\neq} + \varepsilon = 1.1 \pm 0.2\text{eV}. \quad (11)$$

The kink energy on Ag(111) in  $1\text{mM CuSO}_4 + 0.05 \text{ M H}_2\text{SO}_4$  was previously determined by the analysis of the equilibrium shape of monatomic Ag islands to be about  $\varepsilon=0.1\text{eV}$  at

$U_{\text{Ag}}=+60\text{mV}$  vs. SCE [3]. It was also demonstrated that  $\epsilon$  is independent on the electrode potential [2]. Hence, we assume  $\epsilon=0.1\text{eV}$  at  $U_{\text{Ag}}=+50\text{mV}$  vs. SCE, and find

$$E_{\text{ad}}(+50\text{mV}) + E^{\ddagger}(+50\text{mV}) = 1.0 \pm 0.2\text{eV} \quad (11)$$

From the potential dependent analysis of  $F(t)$  on Ag(111) in sulfuric acid at room temperature, where we used a linear ansatz for the potential dependence of the activation energies we found  $E_{\text{ad}}(0\text{mV}) + E^{\ddagger}(0\text{mV}) = 1.0\text{eV}$  [2]. This result is consistent with the number we find from the temperature variable study (eq. (11)). In the case of Ag(111), the use of a linear ansatz for the potential dependence of the activation energies is not only confirmed by our new results but also by calculations by Haftel and Einstein [37]. These authors used the *surface-embedded-atom-model* [38] to determine the dependence of diffusion barriers on the charge deposited on the metal electrode by the electrical double layer. For Ag(111), they show that the diffusion barrier on the terrace is almost charge independent. The diffusion barrier along A-steps depends approximately linearly on the deposited charge. In the case of small variations in the charge (i.e., for small differences in the electrode potential), the functional dependence of the activation energies for atomic mass transport can be approximated by a linear function. In our experiments, the strong potential dependence of  $G(t)$  is limited to a small potential range of about 100mV, and hence, the assumption of a linear dependence of the energies on the potential is justified. As a result one may emphasize that reasonable results for mass transport activation energies may be obtained by temperature dependent measurements also in aqueous electrolytes as well as by the potential dependent studies of step fluctuations at constant temperature, if temperature dependent data is not available. We note, however, that the error bars in both kind of studies are relatively large, at least for experiments performed in aqueous electrolytes, due to the small temperature range available

and the relatively large scattering of the data. The values may serve, nevertheless, as reasonable estimates.

Assuming that the adatom formation energy  $E_{ad}$  for stepped Ag(111) in electrolyte is of the same order of magnitude as for Ag(111) in UHV, we obtain furthermore a reasonable estimate for the activation energy  $E^\ddagger(+50\text{mV})$  of Ag dissolution into the electrolyte. EMT calculations by Stoltze yield  $E_{ad} = 0.62\text{eV}$  [46] in modest agreement with STM investigations by Morgenstern et al. who find  $E_{ad} \sim 0.68\text{eV}$  [47]. Using  $E_{ad} = 0.62\text{eV}$  in eq. (11), one may estimate  $E^\ddagger$  to be about

$$E^\ddagger = 0.4 \pm 0.2\text{eV} \quad (12)$$

We note in passing that it is yet not understood whether activation energies for transport processes and formation energies of surface defects as determined in UHV studies are applicable to metal electrodes in liquid environment. While the kink energy on Ag(111), e.g., is about  $0.1\text{eV}$  in UHV [16] as well as in electrolyte [3], the adatom creation energy and the terrace diffusion barrier may significantly differ from UHV data due to the strong charge dipole associated with a free adatom on the electrode surface. Here, further detailed experimental as well as theoretical studies are desirable.

The pre-exponential factor for Ag dissolution into the electrolyte seems to be considerably larger than the typical value of  $10^{13}\text{ s}^{-1}$  [48] found for hopping rates on surfaces in UHV (although the error bars are quite large). A similar large pre-exponential factor was also found for Cu(111) in chloric acid [39]. One should, however, keep in mind that the typical pre-exponential of  $10^{13}\text{ s}^{-1}$  is known for diffusion processes on solid surfaces under experimental conditions, where desorption into the surrounding gas phase is negligible. For metal electrodes in electrolyte, mass may be exchanged with the liquid phase, i.e., in particular, with

the double layer region, as is the case for Ag(111) in 1mM CuSO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub> at +50mV vs. SCE. And hence, the reason for the high pre-exponential factor could be that the number of degrees of freedom is larger in the double-layer region of the surface [49].

The problem whether the constant contribution to the time correlation function at  $t=0$  is attributed to tip-surface interactions or may have a physical origin remains unsolved. From our measurements we conclude that  $F(t=0)$  is not attributed to an activated microscopic diffusion process which should cause a measurable temperature dependence in the temperature range considered here: Assuming, e.g., that fast back and forth motion of kink atoms as the reason for the constant offset at  $t=0$ , the activation energy should be comparable to the energy for adatom creation from kinks to steps and subsequent diffusion along the steps. In previous measurements on stepped Cu(100) surfaces in UHV [12, 50] an activation energy of about 0.5eV was found for this process. It is reasonable to assume that the energy attributed with this process on a metal electrode in electrolyte should not significantly differ from this value, since no large dipole moment is related to the formation of step adatoms from pre-existing kink sites. Then,  $F(0)$  should vary by a factor of about 3-4 for temperatures between 296 and 311K. Although the scattering of the data in Fig. 4 is large, the fast back and forth motion of kink atoms seems not to be corroborated by our results.

## 6. Summary

We have analyzed the step fluctuations on vicinal Ag(19,19,17) surfaces in a copper containing, aqueous electrolyte as a function of temperature at a constant potential of  $U_{Ag}=+50\text{mV}$  vs. SCE. In agreement with previous potential dependent, room temperature studies on Ag(33,33,31) in the same electrolyte [2], we find that the mass transport is dominated by dissolution of Ag atoms into the electrolyte while no net flux of Ag atoms into the electrolyte occurs. We have demonstrated for the first time that activation energies of atomic mass transport processes on metal electrodes in liquid environment can be measured

by temperature variable studies on step fluctuations. For stepped Ag(111) in sulfuric acid we determined the sum of the activation energy for adatom formation from kinks onto the terrace and for Ag dissolution to  $E_{\text{ad}} + E^{\ddagger} = 1.0 \pm 0.2\text{eV}$ . This result is in agreement with previous room temperature studies where step fluctuations were analyzed as a function of the electrode potential using a linear ansatz for the potential dependence of the activation energies. Our studies demonstrate that reliable information on activation energies for mass transport processes at the solid/liquid interface may be obtained from both, temperature as well as potential dependent studies of step fluctuations.

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### Figure Captions:

**Fig. 1:** The Ag(111) sample is located in an electrochemical cell made from nickel, which is mounted via a magnetic support to the microscope socket. The electrochemical cell is sealed by a chemically resistant ring and a PTFE lid, which also holds reference and counter electrode. The Peltier element is located in the socket, enabling heating and cooling of the electrochemical cell and the sample.

**Fig. 2:** Temperature calibration of the heating and cooling device. The sample temperature  $T_s$  is a linear function of the reference temperature  $T_0$  and was measured in thermal equilibrium via a thermocouple connected to the electrode surface.

**Fig. 3:** Time image of a stepped Ag(19 19 17) surface at  $T=296$  K and an electrode potential of +50 mV vs. SCE. The axis perpendicular to the step direction is a spatial axis, whereas the axis parallel to the steps is a time axis. The scan width is 40 nm and the scan time of the whole image is 21 s.

**Fig. 4:** Correlation value  $F(t_0)$  at  $t_0=0$ s as a function of the electrode temperature. The unit of  $F(t_0)$  is given in kink length squared. Despite some scattering no systematic dependence of  $F(0s)$  is observed in the experimental temperature range.

**Fig. 5:** Time correlation functions  $F(t)$  as measured for  $T_s=296, 302$  and  $307$ K. The step fluctuations increase with increasing sample temperature. The solid lines are least square fits to eq.(8) with the constant offset  $F(0)$  at  $t=0$ s subtracted.

**Fig. 6:** Arrhenius plot of the correlation value  $F(t_0=2s)$  at constant electrode potential +50mV vs. SCE. The data points were obtained from different surface regions of several Ag samples with the same nominal vicinal orientation, however, revealing locally different step densities. In order to display the data within the same view graph, the data was scaled by the square root of the step-step distance (in units of  $a_{\perp}$ ).

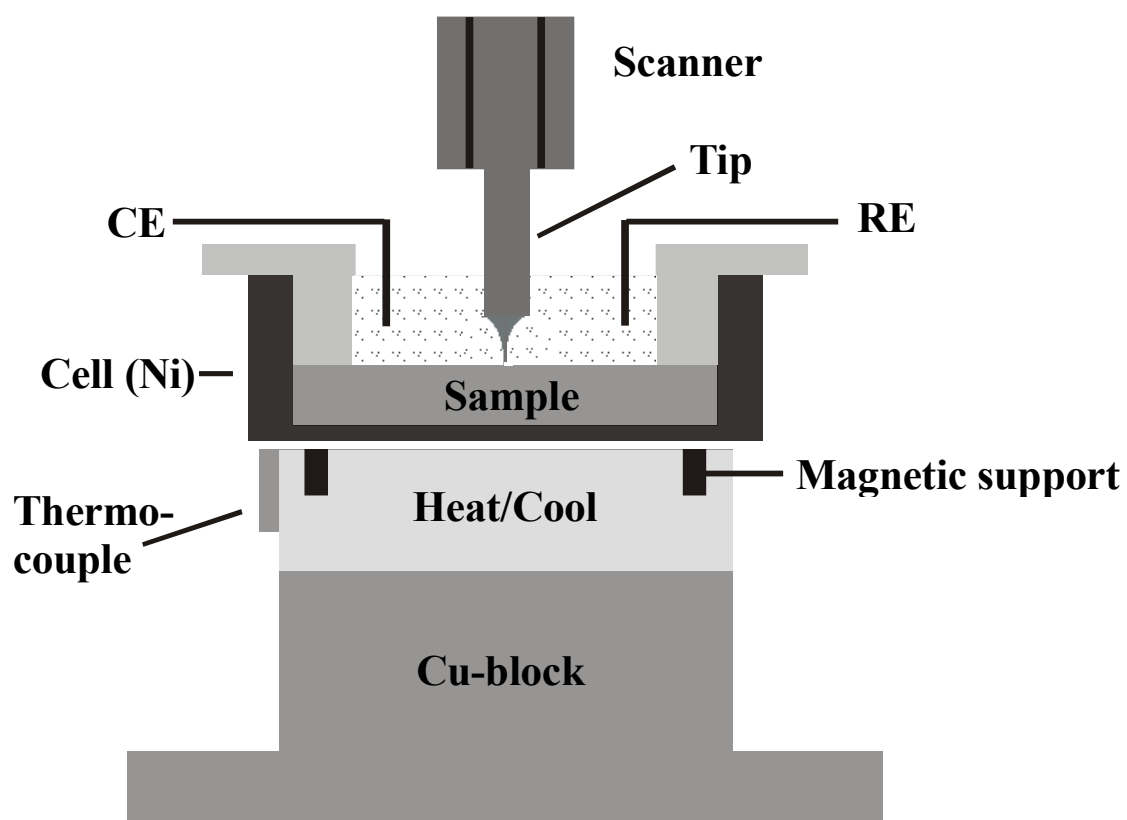
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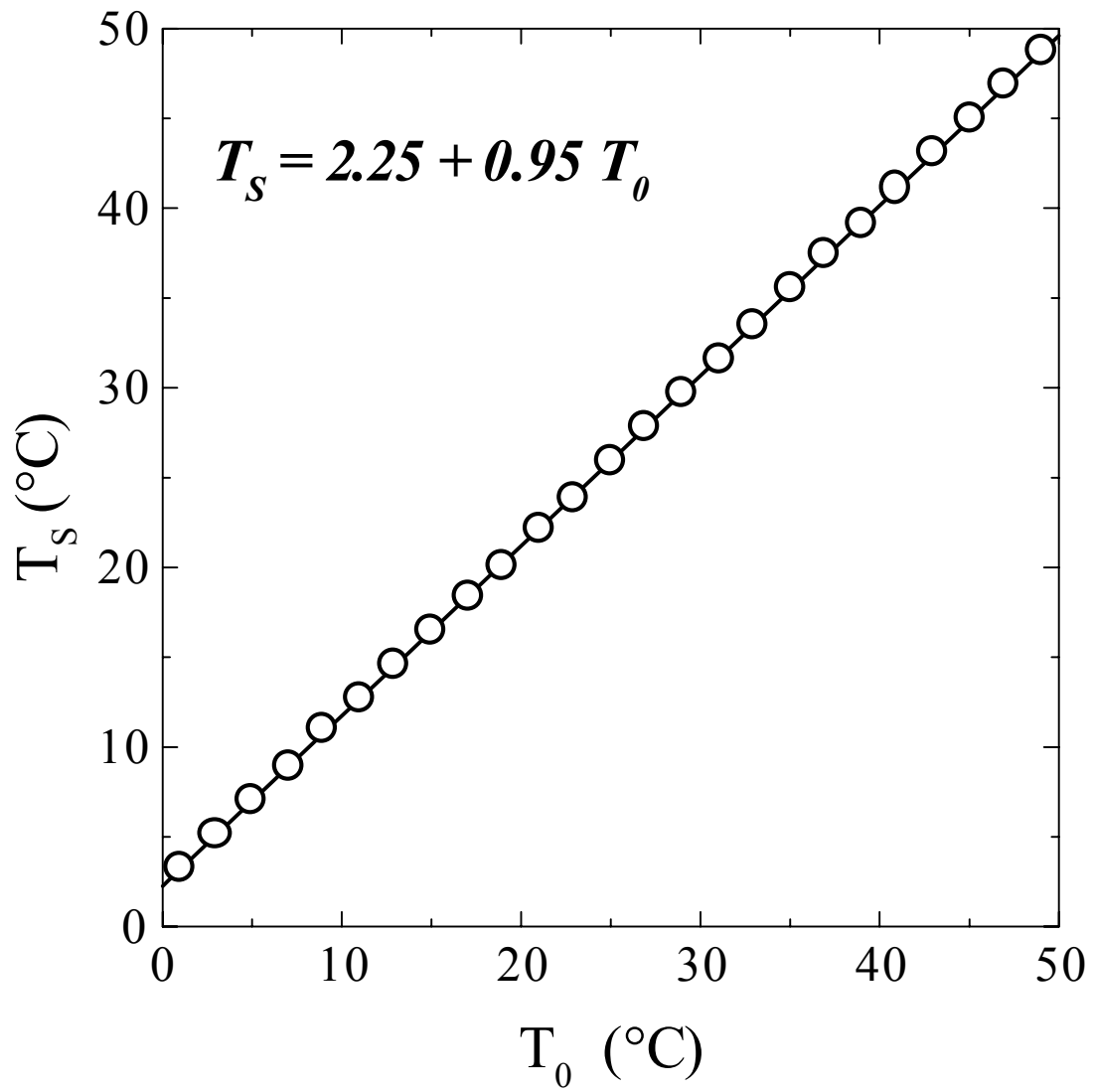
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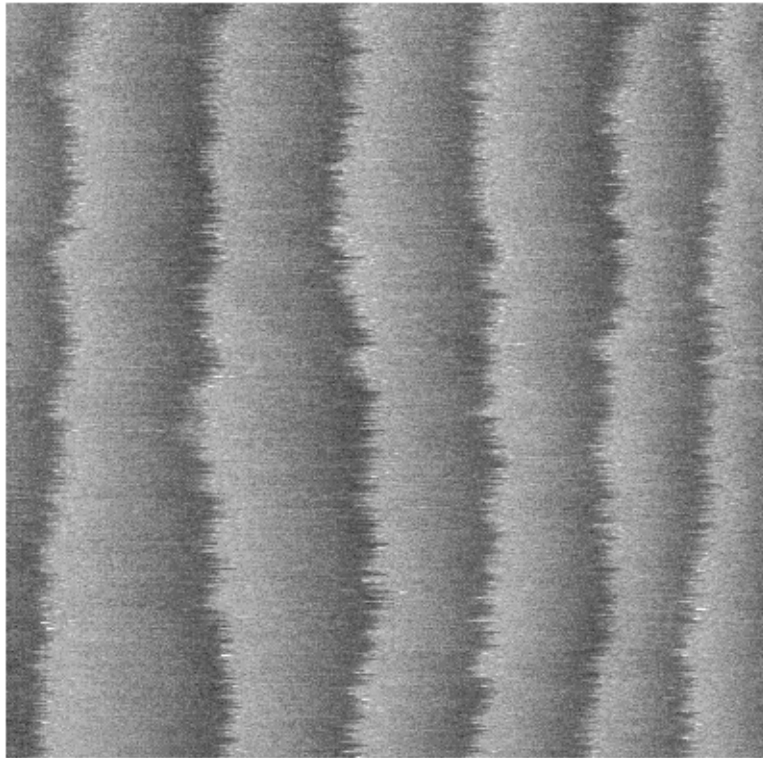


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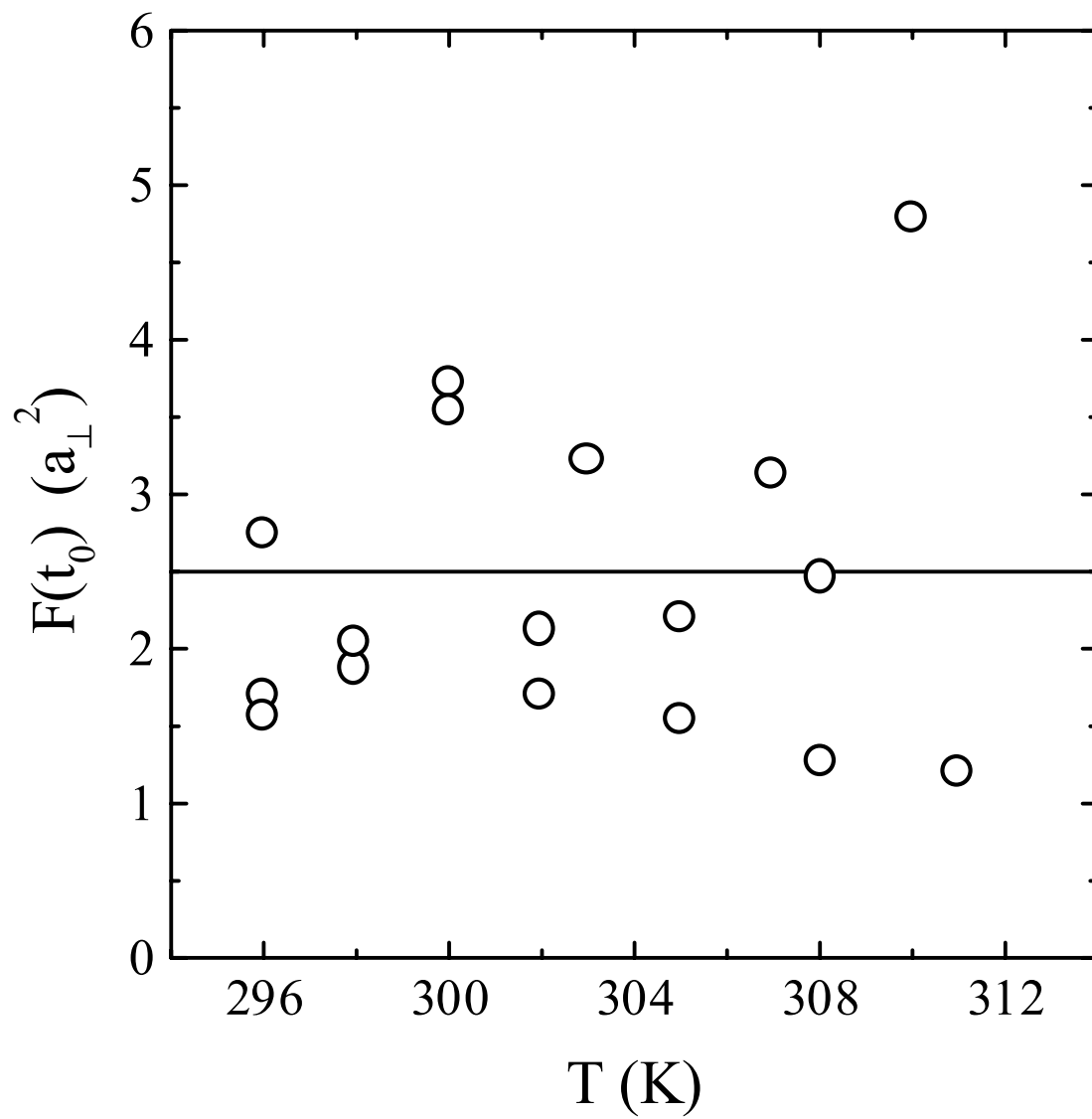
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**Fig. 1**

**Fig. 2**



**Fig. 3**

**Fig. 4**

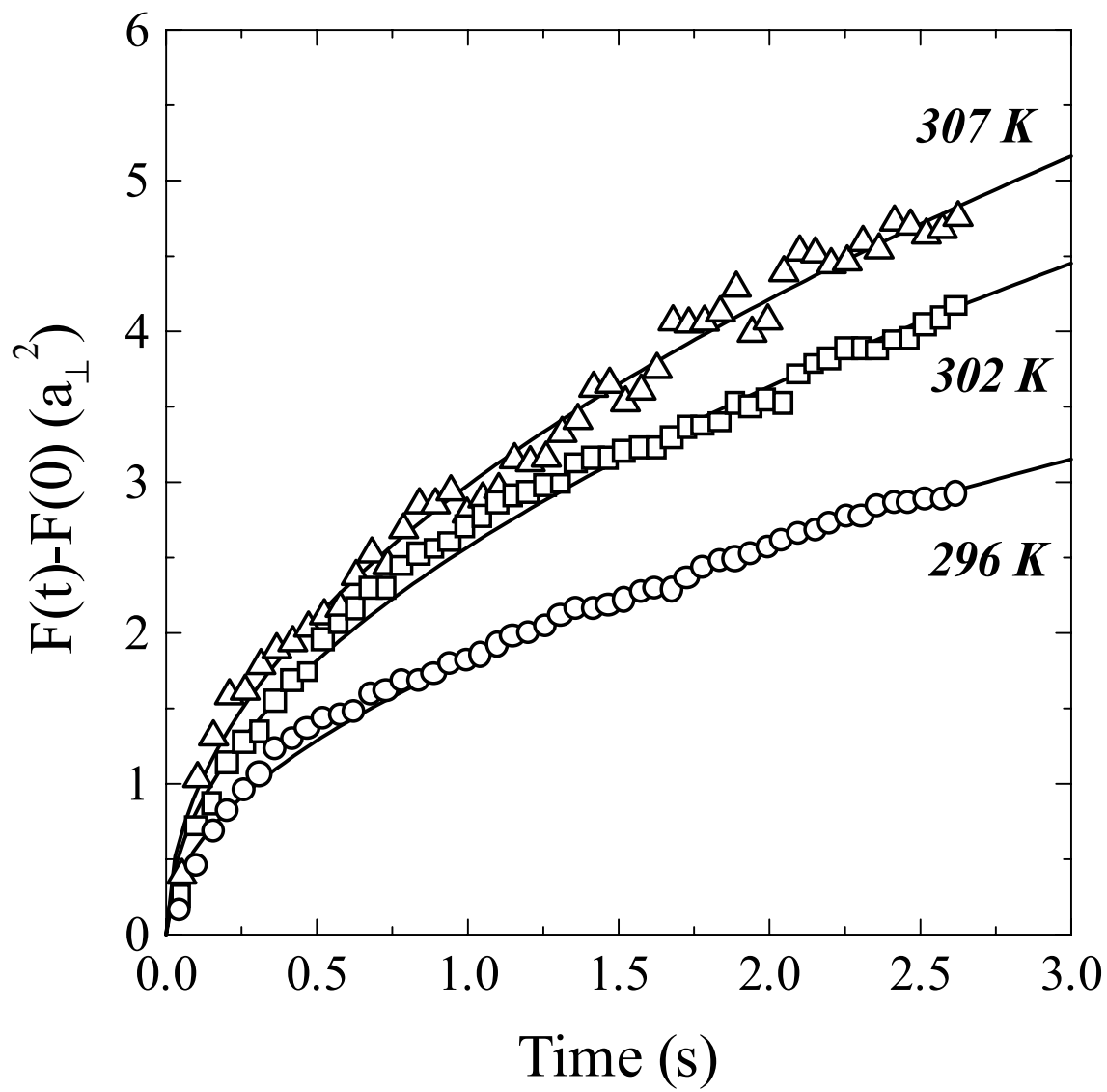


Fig. 5

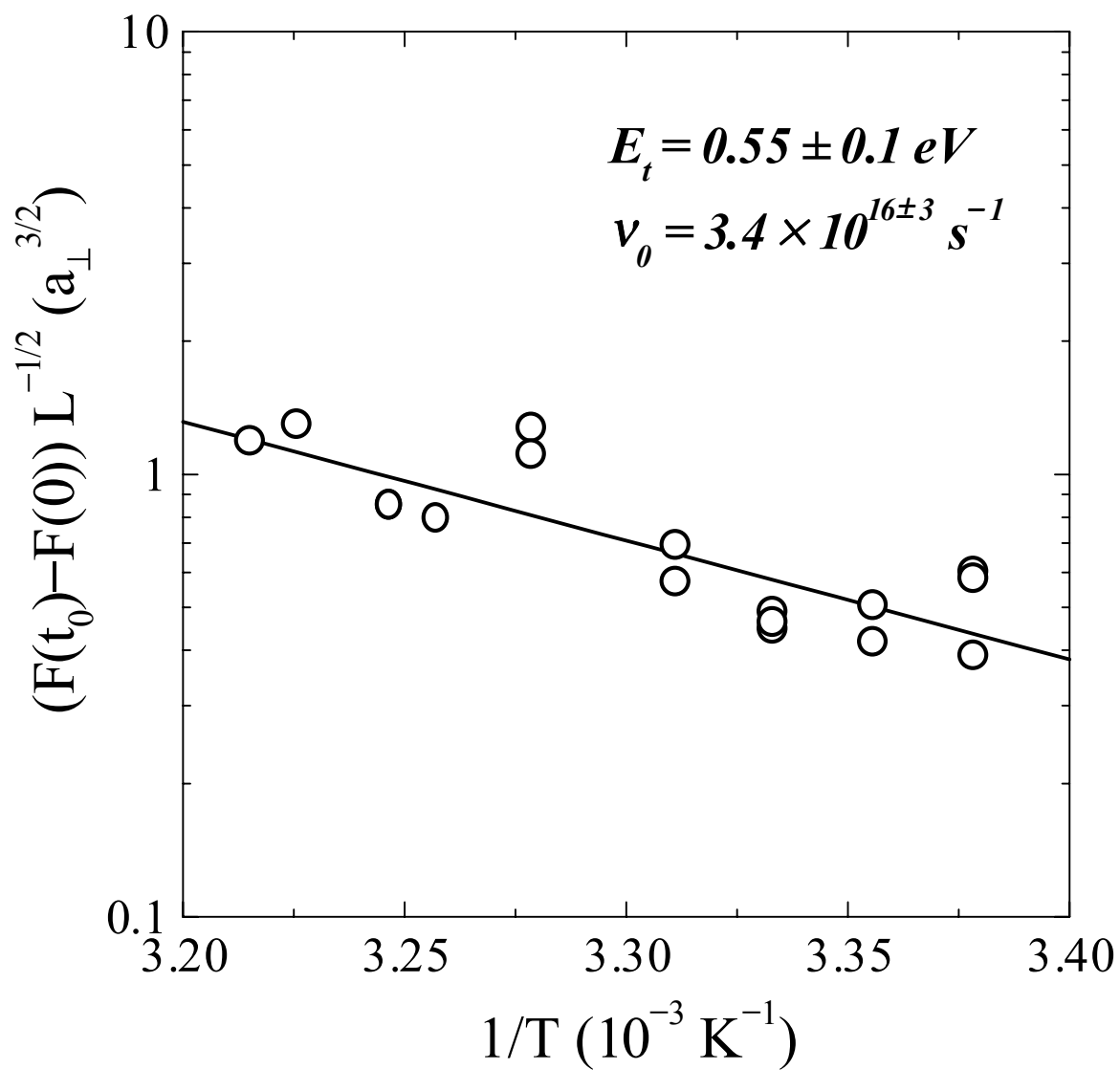


Fig. 6