NMR Observation of Diffusion Barriers for Lithium Adsorbed on Ru(001)

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The diffusion of lithium on a Ru(001) surface has been studied with nuclear magnetic resonance techniques using the radioactive isotope ^{8}Li as a probe. As a function of substrate temperature and alkali metal coverage the nuclear spin-lattice relaxation measurements show the existence of two distinctly different diffusion barriers on the surface, valued at 0.46 and 0.22 eV. The former is attributed to jumps from step to terrace sites, whereas the latter is the barrier between adjacent terrace sites. At 200 K the Li diffusion was observed from low to full coverage.

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Surface diffusion (SD) is one of the most fundamental surface phenomena, and has been a subject of scientific interest since the very beginning of surface investigations [1,2]. Essentially all dynamical processes occurring at a surface are strongly dependent on SD, be it crystal growth, epitaxy, or chemical reactions. Even "simple" processes like adsorption or desorption involve often SD mediated steps. More complicated phenomena like catalytic reactions cannot be understood without substantial knowledge of the temperature and morphology dependence of the underlying mass transport processes. Compared to its importance, the amount of available experimental material and the insight in details of the mass transport process is rather small [3]. Because of the presence of steps, kinks, vacancy sites, and the like on every real crystal surface a large variety of single jump processes exists on a microscopical scale besides the jumps between neighboring terrace sites [4]. Especially these defect sites influence the above mentioned complex dynamical processes strongly. On a macroscopical scale the various single jump processes yield a strongly temperature and surface morphology dependent motion [5]. The interpretation of such motion is complicated by the fact that every crystal has an individual misorientation, grain boundary morphology, and growth failure distribution, making the comparison of results, obtained often with different experimental techniques, difficult.

Here we present an investigation of the microscopical diffusion of lithium on Ru(001) with a nuclear magnetic resonance (NMR) method. NMR has proven to be a powerful technique to study transport phenomena in solid state physics [6]. In our context the spin-lattice relaxation driven by the fluctuating nature of the interaction between the nucleus and its surrounding electromagnetic field due to atomic motion is used to probe diffusion. We use a suitably adapted technique (β-NMR, [7]) utilizing the properties of the radioactive isotope ^{8}Li (half-life $T_{1/2} = 0.84$ s, nuclear spin $I = 2$). The latter represents the important class of alkali adsorbates, which are accessible to NMR investigations on single crystal surfaces. For this novel experiment the well-studied transition metal substrate Ru(001) was chosen for practical purposes.

The application of NMR techniques to single crystal surface problems is not straightforward because the sensitivity of conventional techniques is completely insufficient. Here we adopt a mixed technique of β-radiation detected NMR (β-NMR) and atomic beam methods to gain highly magnetized nuclear ensembles on a surface. The β-NMR has been applied in solid state physics [7] for some time. It utilizes the parity violating forward/backward asymmetry of the electron emission in a β decay to detect nuclear magnetization. The ^{8}Li isotope we use is produced in the nuclear reaction $d(^7\mathrm{Li}, ^8\mathrm{Li})p$ from a 24 MeV $^7\mathrm{Li}^{3+}$ ion beam. To ensure a gentle "landing" on the Ru(001) surface and not an implantation of the ^{8}Li the fast reaction product is thermalized by implanting it into a graphite stopper, from which it is evaporated thermally. The thermal atomic beam thus formed is highly polarized by the application of laser optical pumping, a Stern-Gerlach sextupole magnet, and radio frequency transition techniques. The atomic beam delivers about 5000 ^{8}Li atoms/s to the surface with a nuclear polarization of 0.6 to 0.8. This yields an initial count rate of about 500/s and asymmetries of up to 0.2. The ^{8}Li beam is accompanied by a 4 orders of magnitude more "intense" also thermalized beam of ^{7}Li. But this is still low enough that experiments can be carried out under very dilute conditions unless additional lithium is supplied from a getter source. A detailed description of the ^{8}Li source and the UHV setup can be found elsewhere [8,9].

The UHV surface analysis chamber employs Auger spectroscopy (AES), low energy electron diffraction (LEED), temperature programed desorption (TPD), a Kelvin probe for work function measurements ($\Delta\Phi$), several Li and gas dosers, and a special section for the β-decay detection in an external magnetic field. The base pressure is 5×10^{-11} mbar. During the ^{8}Li experimental sessions frequent cleaning cycles in the rather narrow β-detection section leads to an increased pressure of 3×10^{-10} mbar. The TPD and $\Delta\Phi$ of Li/Ru(001) follows the behavior given in the literature, no indication of Li diffusion into the bulk is known [10–12]. We characterize a Li monolayer (ML) by the onset of a zero order low temperature "multilayer" TPD peak.

The nuclear spin relaxation rate was obtained by measuring the time dependence of the β-decay spatial asymmetry. Figure 1 shows the raw data of the spin relaxation of ^{8}Li on a Ru(001) surface at 200 K which has been recovered with 0.92 ML of lithium. The results were fitted by a single exponential, the decay constant being the sought after relaxation rate; it is 2.5 ± 0.5 s^{-1} in this case. In all presented data at least an amount of 0.02 monolayer had been added, to occupy defect sites. We found that experiments with very little or no additional lithium coverage (i.e., below 0.001 ML) showed preparation-dependent uncontrollable behavior [13,14].

The temperature dependence of the nuclear spin relaxation rate, which has been published recently [14], was measured in the range from 200 to 1250 K and is shown in Fig. 2. Two main features can be seen. Firstly there is an underlying contribution to the relaxation rate that is linear in temperature. It is caused by the "Fermi contact" interaction of the magnetic moments of the delocalized metal electrons with the nuclear moments (Korringa relaxation) [6,15]. The rate bears information on the local density of states at the Fermi energy and was discussed recently [14]. The second obvious feature seen in the data in Fig. 2, which is addressed in this paper, is the strong increase between 300 and 600 K attributed to diffusion. Fluctuations of the interaction between the nuclear quadrupole moment of ^{8}Li [16] and the surrounding electric field gradient (EFG) lead to transitions between the spin substates and therefore the level populations can reach thermal equilibrium (nuclear spin relaxation) [6,7,15]. Such fluctuations are introduced by the atomic motion across the surface. Mathematically the Fourier transform of the autocorrelation function of the time dependent part of the Hamiltonian, i.e., the spectral density, gives the frequency spectrum of the field fluctuations. Evaluation of this spectrum at the resonance (Larmor) frequency ω_L of the nuclear spin gives the nuclear spin relaxation rate α [6]. This concept leads to a quasiresonant temperature dependence of the relaxation rate, if one assumes that the correlation time τ_c is related to diffusion [7,17] and thermally activated,

$$\tau_c = \tau_0 \exp(E_{\mathrm{diff}}/kT)\,. \qquad (1)$$

Here E_{diff} denotes the diffusion energy and τ_0 a time prefactor. At low temperature the spectrum is restricted to frequencies below the Larmor frequency. At high temperature the spectrum extends over a vast frequency range with a low spectral density at ω_L. At an intermediate temperature ($\omega_L \tau_c \approx 1$) the spectral density and therefore the relaxation rate reach a maximum. This is what can be seen in Fig. 2. The solid line is a best fit resulting from an empirical model for the relaxation rate, which has been successfully used in two-dimensional systems [18,19]:

$$\alpha = G\tau_c \ln[1 + (\omega_L \tau_c)^{-2}]\,. \qquad (2)$$

G stands for the strength of the interaction of the nuclear moments with the local electric field gradient. (Dipolar diffusional relaxation is omitted, because of the small nuclear moments of the ruthenium isotopes and the strong quadrupolar interaction of ^{8}Li on surfaces [20,21].) The fit gives $\tau_0 = 10^{-13\pm1}$ s, $E_{\mathrm{diff}} = 0.46 \pm 0.02$ eV, and a value for G which is compatible with an EFG of 10^{16} V/cm^2. The errors given are estimated from values leading to a "bad" data representation in the fitting procedure. The discussion of the values is postponed.

Figure 3 shows relaxation rates at fixed temperatures of 200 and 800 K as a function of the alkali metal coverage. The maximum coverage at 800 K is limited by thermal desorption to about 0.15 ML. The fact that there is no variation in the relaxation rate at 800 K shows that the relaxation processes are not influenced by the interaction

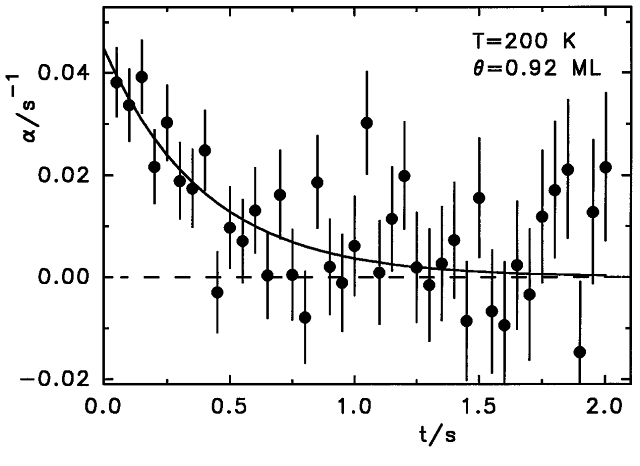

FIG. 1. ^{8}Li β-decay count rate asymmetry as a function of time. The surface was covered with 0.9 ML of stable lithium. The solid line is a single exponential with the decay constant, i.e., relaxation rate $\alpha = 2.5$ s^{-1}.

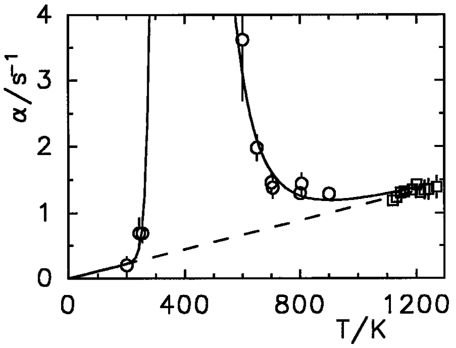

FIG. 2. The nuclear spin lattice relaxation rate α as a function of the surface temperature. The dashed line gives the Fermi contact part of the relaxation, whereas the solid line includes the diffusional relaxation.

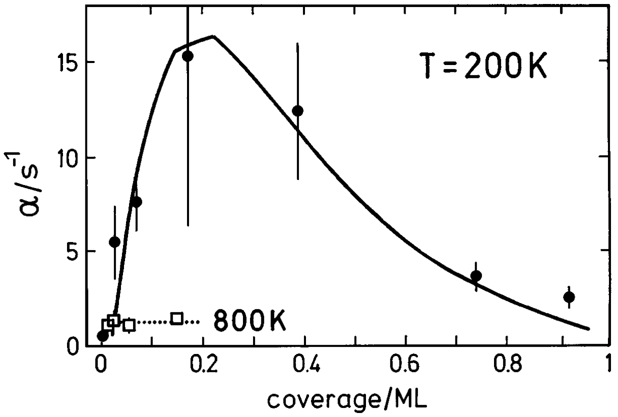

FIG. 3. Spin lattice relaxation rate α as a function of lithium coverage at two different surface temperatures. The solid line shows the result of a Monte Carlo simulation of the hopping process including Li-Li interaction. The dotted line represents the average value of the 800 K data, since the data show no coverage dependence (the error bars are about the symbol size).

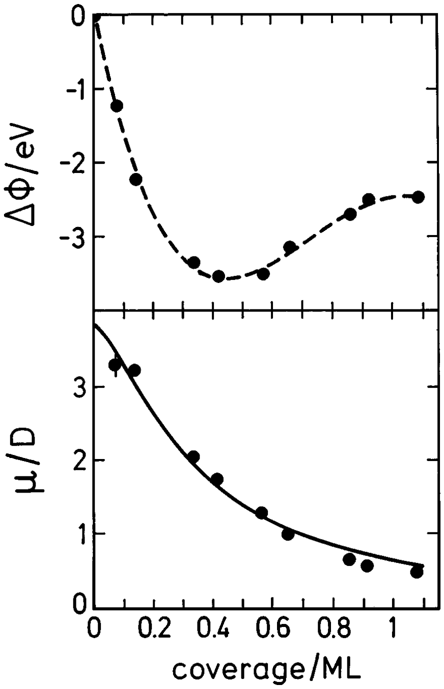

FIG. 4. Work function change as a function of lithium coverage (upper figure) and resulting dipole moment μ per lithium atom (lower figure).

between the lithium atoms at this temperature. At 200 K the situation is very different. From the strong increase of the relaxation rate with coverage we conclude that the fluctuating part of the adsorbate-adsorbate interaction, i.e., terrace diffusion, causes the relaxation. The low temperature indicates that the barrier must be significantly lower than the one obtained from Fig. 2.

The interpretation of these results requires the discussion of the kind of fluctuations a probe atom will experience at different coverage levels. The motion across the flat (001) surface should not cause fluctuations of the electric field gradient, if the atoms jump in between equivalent adsorption sites in the limit of zero coverage. The jump process itself should not influence the relaxation since it takes place on a very different time scale (10^{-12} to 10^{-14} s) as compared to the Larmor precession period in an external magnetic field of 66 mT ($\approx 10^{-6}$ s). However, the surface contains most certainly a variety of defect sites, from which the step site should be the most abundant one. The binding geometry of a lithium atom at the step (or any other defect) and thus the electric field gradient is very different from the one on a terrace site [22]. Diffusion between these sites causes therefore strong fluctuations in the quadrupolar interaction Hamiltonian and thus nuclear spin relaxation. We believe that this scenario is observed in the relaxation rates from Fig. 2. The energy of 0.46 eV is of reasonable magnitude for such a step-to-terrace barrier. The term "step site" just represents an abundant defect site. Because of the presence of 0.02 ML of lithium during the measurement strongly binding rare sites should be occupied at all times. Therefore we think that the step site is most likely the real step site.

At higher adsorbate coverages the interaction between the alkali metal atoms has to be taken into account. It is well known that the adsorption of an alkali metal atom on a metal surface leads to a local electric dipole moment, responsible for the strong work function changes [23]. Therefore at higher coverages a ^{8}Li probe atom will sense fluctuations of EFG during diffusion also on the (001) terraces, introduced by neighboring alkali metal atoms. Assuming the dominance of this kind of field fluctuation, the coverage dependence of the relaxation data from Fig. 3 can be described by a rather simple Monte Carlo model. To calculate the magnitude of the EFG at a neighboring adsorption site, the magnitude of the local dipole moment, caused by an alkali metal atom, is required. This quantity is accessible from work function measurements. In the upper part of Fig. 4 the change in work function for Li/Ru(001), measured with a Kelvin probe [24] is plotted as a function of alkali metal coverage. The dashed line serves to guide the eye. From these data a mean coverage dependent local dipole moment μ can be extracted by using the Topping model [23]. In the lower panel of Fig. 4 the resulting average dipole moment is given along with an interpolation (solid line) obtained from the model. The distance between two neighboring lithium atoms at close proximity has been taken from TPD and a LEED investigation of the $\sqrt{3} \times \sqrt{3}$ superstructure [12]. Within the Monte Carlo model the lithium atoms undergo a random walk on a square lattice where occupied neighboring sites block diffusion. The electric field gradient fluctuation taken into account is the one caused by next neighbor alkali metal atoms, the distribution of which changes during the random walk. Long range interactions sum up to a time independent contribution and therefore are of no consequence for relaxation. The only adjustable parameter is the mean residence time τ on a terrace site, which is given as $\tau = \tau_0 \exp(-E_{\mathrm{diff}}/kT)$ with an assumed 10^{-13} s as a prefactor and an adjustable diffusion energy. [The step-to-terrace barrier of 0.46 eV does not enter this model, since at 200 K the mean residence time at such a higher binding site is too long (≈ 0.04 s) to cause significant relaxation.]

The Fourier transform of the calculated time correlation function of the interaction evaluated at the resonance frequency yields the relaxation rate. The solid line in Fig. 3 shows the results of the model, which reproduce the form and magnitude of the experimental relaxation rate with a diffusion energy of 0.22 eV. Using a lattice spacing of $a = 2.7$ Å a diffusion constant [3] for motion on the terrace of $D(200\ \mathrm{K}) = a^2/4\tau = 5 \times 10^{-9}\ \mathrm{cm}^2/\mathrm{s}$ can be inferred at low coverage. At higher coverages the diffusion constant is much reduced due to the site blocking effect. Using the model parameters at 800 K no coverage dependence could be seen in accordance with the data (Fig. 3). This is not surprising, since the high temperature reduces the mean residence time on a single terrace site to around 10^{-11} s, which effectively eliminates this relaxation process.

It should be noted that the two barriers found are certainly always present on the surface at the same time. The NMR experiment, however, is sensitive to the one or the other dependent on the temperature and coverage. A comparison to other experiments on the same system is not possible due to the lack of data, both barriers found are, however, in the range of surface diffusion energies [3]. The results show the severe complications in the analysis of diffusion data even in the *microscopic* regime, since the presence of more than one barrier has to be expected in virtually all systems.

Because of the high sensitivity of our nuclear magnetic resonance technique we were able to investigate the lithium diffusion in a homogeneous alkali metal adlayer in two coverage regimes. In a temperature dependent measurement at low coverage a diffusion barrier of 0.46 eV was observed, probably the activation energy to cross or leave a surface step. At higher coverages the adatom diffusion on the terraces becomes visible. Here the fluctuations of the Li-Li electrostatic interaction are found responsible for the observed relaxation. In a Monte Carlo simulation an energy of 0.22 eV for the terrace diffusion barrier is found.

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