Coverage Dependence of the Local Density of States at the Fermi Energy: Li Adsorbed on Ru(001)

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The local density of states (LDOS) of Li on a Ru surface has been determined between very low and 0.15 monolayer coverage. β-decay detected nuclear magnetic resonance has been employed to measure the spin lattice relaxation rate between 200 and 1250 K. The $\mathrm{LDOS}(E_F, 0) = 0.13(1)\ \mathrm{eV}^{-1}\ \text{Å}^{-3}$, which is 0.6 of the bulk metallic value supporting a view of an at most weak ionic bond. No coverage dependence of the LDOS is seen in the regime investigated. Thus the adsorbate wave functions do not overlap. The LDOS provides a benchmark against which theoretical approaches must be measured.

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The question of the "nature" of the alkali atom bond towards a substrate in adsorption systems is still heavily debated although the problem has received a considerable amount of attention. The early picture of Langmuir and Gurney [1] of an ionic bond has been under strong discussion since the advent of modern *ab initio* density functional calculations [2–4]. Many experimental as well as theoretical investigations have been performed to tackle the problem [5]. Recently, precise core level shift measurements of alkali adsorbates and substrates were interpreted in a picture of strong covalency [6], an interpretation that was seriously challenged since Refs. [4,7]. The very physical concept of charge state is often used, but it creates a problem on the theoretical side due to the lack of a quantum mechanical operator for it. The interpretation of experimental results in terms of charge state, ionicity, or covalency is certainly hampered by this but also complicated by the many mechanisms that often contribute to a single observable. As an example, x-ray photoelectron spectroscopy is mentioned with their various contributions to the binding energy shifts [6,7]. This is similarly true for metastable deexcitation spectroscopy [8] or the scattering and neutralization of deuterium ions [9].

The local density of states (LDOS) is an appropriate quantity to describe the nature of an adsorbed atom's bond. The substrate and adsorbate structure enter in this quantity. The LDOS is an energy and position dependent measure of the electronic structure. Here *local* is understood as a *point* quantity and not as an integral over some atomic size volume, as is sometimes done. In NMR experiments the LDOS at the Fermi level and at the nucleus investigated enters in the Knight shift and in the longitudinal relaxation (T_1 times) for metallic systems [10]. The $\mathrm{LDOS}(E_F, r = 0)$ can be determined in a straightforward manner as an *absolute* quantity and can thus provide a benchmark against which theoretical approaches must be measured [11].

Here we present a novel experimental approach in which a coverage dependent measurement of the $\mathrm{LDOS}(E_F, r = 0)$ at a lithium adsorbate on Ru(001) is performed by a suitably adapted solid state NMR technique. Korringa and many authors after him [10] investigated the spin lattice or longitudinal relaxation behavior of nuclear spins in metals. In s-state dominated systems the main electronic relaxation is caused by Fermi contact interaction of the nucleus with the electronic spins. The necessary mutual spin flip of the nucleus and an electron can occur only with electrons at the Fermi level. The contact part ensures the local nature of the interaction. The widely accepted view of this process is that a nonequilibrium nuclear magnetization returns to its thermal value by a rate $\alpha = 1/T_1$ that is given by [10,12]

$$\alpha = \frac{256\pi^3}{9}\,\mu_e^2\left(\frac{\mu_n}{I}\right)^2 \mathrm{LDOS}(E_F, 0)^2\,\frac{kT}{\hbar}\,. \qquad (1)$$

Apart from the moments, the temperature, and constants the formula only contains the LDOS as an unknown quantity, which can thus be determined from the measured α without the need for additional theory. The important prerequisite of this procedure is that the spin lattice relaxation is indeed dominated by the Korringa relaxation. This is experimentally identified by the linear dependence of α with the substrate temperature. Thus we interpret a relaxation rate that is linear in temperature as being due to the process described in formula (1).

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 [13] for some time. It utilizes the parity violating forward/backward asymmetry of the electron emission in β decay to detect nuclear magnetization. The ^{8}Li isotope we use is produced in the nuclear reaction $d(^7\mathrm{Li}, ^8\mathrm{Li})p$

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from a 24 MeV ^{7}Li 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 magnetized by laser optical pumping, Stern-Gerlach sextupole magnets, 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" beam of ^{7}Li (also thermalized). But this is still so low 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 [14]. 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 lead to an increased pressure of 3×10^{-10} mbar. The TPD and $\Delta\Phi$ of Li/Ru(001) follow the behavior given in the literature [15,16]. We characterize a Li monolayer by the onset of a zero order low temperature "multilayer" TDS 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 relaxation of ^{8}Li on a Ru(001) surface at 800 K, which has been precovered with an additional 0.02 monolayer of lithium. The results were fitted by a single exponential, the decay constant of which is the sought after relaxation rate; it is 1.35 s^{-1} in this case. The added amount of 0.02 monolayer serves to occupy defect sites. We found that experiments with very little or no additional lithium coverage (i.e., below 0.001 monolayer) showed preparation-dependent uncontrollable behavior [17]. Figure 2 shows a series of TPD spectra of Li/Ru(001) in a coverage range of 0.001 to 0.02. All the individual traces have the same shape and peak temperature. From this we conclude that up to 0.02 monolayer no interaction of the lithium adsorbates occurs [5].

The temperature dependence of the nuclear spin relaxation rate was measured in the range from 200 to 1250 K and is shown in Fig. 3. The data between 200 and 900 K were obtained using ^{8}Li and the β-decay method described above. The data between 1100 and 1250 K were measured with the stable isotope ^{6}Li as a probe using a laser spectroscopic technique suitable only at high temperatures [18,19]. The two sets of data, although obtained with different techniques in different laboratories, complement each other remarkably well. Two main features can be seen in Fig. 3. Firstly, there is an underlying contribution to the relaxation rate that is linear in temperature. Secondly, a peaked resonancelike structure is obvious between 300 and 600 K. This latter effect is due to diffusion induced relaxation and will be dealt with in a forthcoming paper [20]. On the high temperature side of the peak this relaxation mechanism is no longer effective, since diffusion occurs on a much faster time scale than the nuclear Larmor precession [10]. The linear part in Fig. 3 identifies the relaxation process as being due to the conduction electrons, thus formula (1) can be used directly to obtain the local density of states, which is $\mathrm{LDOS}(E_F, 0) = 0.13(1)\ \mathrm{eV}^{-1}\,\text{Å}^{-3}$ at the lithium adsorbate. The error quoted is the "fitting" error that is derived from the data analysis within the model that describes the relaxation process as being due to Korringa and diffusional relaxations. A systematic error containing an estimate on the validity of the model can hardly be obtained, except that with the omission of the linear part no reasonable description of the data is possible and that both *Korringa* and *diffusional* relaxation contributions *must* be present. In this spirit the data analysis uses a minimum number of parameters and concepts. Comparing the obtained value of the LDOS of lithium at the surface to that within lithium metal [10,21] one obtains

$$\frac{\mathrm{LDOS(Li\ on\ Ru)}}{\mathrm{LDOS(Li\ in\ Li\ metal)}} = 0.6. \qquad (2)$$

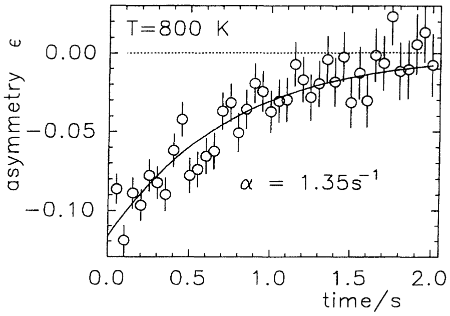

FIG. 1. ^{8}Li β-decay count rate asymmetry $\epsilon = [N(0°) - N(180°)]/[N(0°) + N(180°)]$ as a function of time. The solid line is a single exponential with the decay constant, i.e., relaxation rate, $\alpha = 1.35\ \mathrm{s}^{-1}$.

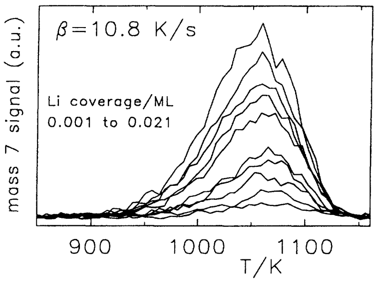

FIG. 2. Thermal desorption spectra of lithium on Ru(001) at very low coverages. The heating rate is $\beta = 10.8$ K/s. Spectra from bottom to top belong to different initial coverages about equally spaced between 0.001 and 0.021 monolayer.

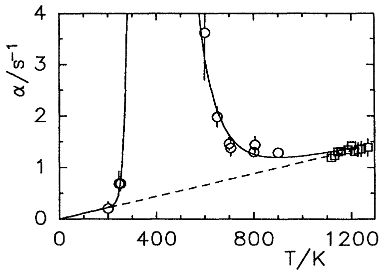

FIG. 3. The nuclear spin lattice relaxation rate α as a function of temperature. Circles denote the data obtained from ^{8}Li decay (Li coverage 0.02 monolayer) squares from ^{6}Li relaxation [18,19]. The solid line gives the sum of a diffusional relaxation and the Fermi-contact part [20]. The latter part is given by the dashed line.

This means that Li on the transition metal ruthenium retains a large fraction of its metallic character, but it also deviates from it. The result suggests that a highly ionic view of the surface complex is not called for. Since Li in lithium metal is neutral, it is tempting to infer a degree of ionicity from (2). This is not possible, since the LDOS is *local* in space and energy and the charge on an atom, however it is defined, is an *integral* quantity involving some volume and energy integration of LDOS(E, r).

One of the important features of alkali adsorption on metals is the strong coverage dependence of the work function and the binding energy. Therefore we performed a coverage dependent measurement of the LDOS. A temperature of 800 K was chosen as a compromise. A still present diffusional contribution to the relaxation rate is thought to be small enough and not coverage dependent, since it is most likely caused by the step terrace diffusion barrier [20]. At 800 K Li coverages up to 0.15 monolayer could be prepared. Higher coverages desorb during the experimental cycle of about 5 min. At 200 K (the lowest currently feasible temperature) diffusion still dominates the relaxation for all but the smallest coverages [20]. At a coverage of 0.15 monolayer the work function is already reduced by 2.5 eV [Fig. 4(b)] and the TPD peak temperature has shifted by about 150 K. Thus a rather strong interaction between the adsorbates already occurs. Figure 4(a) shows the relaxation rate measured at 800 K for several coverages up to 0.15 monolayer. The intriguing result is that experimentally no coverage dependence can be seen. This also means that the LDOS is constant up to this coverage. From this one can conclude that no wave function overlap of the adsorbates occurs, because an overlap should have the largest effect for most extended states, i.e., the least bound at the Fermi level, and thus be observed by a change in the LDOS.

Unfortunately, no theoretical calculations are available up to now to which the experimental results could be compared quantitatively. Recently, the density functional approach has been used to calculate the LDOS($E_F, r = 0$) and therefore the nuclear spin relaxation rate of Li on "jellium" [12], but not yet on a structured substrate.

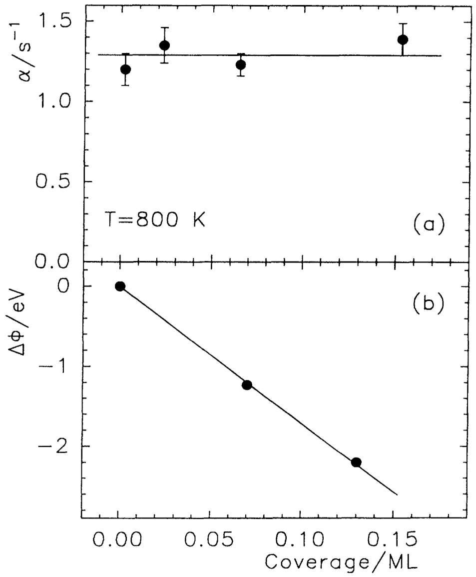

FIG. 4. (a) Spin lattice relaxation rate α as a function of lithium coverage on a surface given in monolayers. (b) The work function change under the same condition.

The nil result of the coverage dependence of the LDOS has to be discussed together with the strong change in work function and the considerable reduction of the desorption temperature in TPD. The reduction of the work function with coverage is still strictly linear in the coverage regime accessible, as can be seen in Fig. 4(b) or in [16]. This is understood as the result of a constant electric dipole moment per alkali adatom [5], which adds up to a work function change proportional to the coverage. In agreement with the LDOS result a depolarization of the electric dipoles due to their mutual interaction has not occurred. The second effect of the reduction in the TPD temperatures even at much smaller coverages than 0.15 monolayer is very typical for adsorbed alkali atoms [5]. It is explained by the mutual repulsion of the electrostatic dipoles [5]. Both effects thus agree with the conclusion of an unaltered adsorption state in the observed coverage regime.

The local density of states at the Fermi level and its coverage dependence provide experimental results that are, by nature of the NMR technique used, rather well defined. Comparison of the Li/Ru(001) result to the bulk one shows that the Li state of adsorption retains strong although not complete metallic character. From the constancy of the LDOS we conclude that the wave function describing the adsorbate is unchanged up to a coverage of at least 0.15 monolayer.

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