

Electron correlations in the clean and hydrogen-covered Si(111)-(7×7) surface at extremely low Li coverages

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The observation of “Korringa” nuclear spin relaxation (spin-lattice relaxation) of ^8Li probe atoms, adsorbed at extremely low coverages (below 10^{-5} ML) on the Si(111)-(7×7) surface points to the existence of a highly correlated two-dimensional electron gas at this surface (“metallic” surface). The observed large relaxation rates, as compared to Li adsorption on metals, is interpreted as an interplay of longer correlation times and a reduction of electronic density of states. Surprisingly, relaxation rates, linear in temperature and independent of magnetic field were observed for Li adsorbed on a hydrogen-covered Si(111)-(7×7) surface also. Various explanations for this surprising and puzzling result are discussed.

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I. INTRODUCTION

Since its discovery¹ in 1959 the (7×7) reconstructed Si(111) surface has received quite some attention within the surface sciences, earlier mainly experimentally, but in recent years due to increasing computing power also theoretically. The surface electronic properties have been analyzed experimentally with various techniques. Photoemission experiments revealed density of states at the Fermi level [DOS(E_F)] caused by a surface state (S_1) 0.2 to 0.3 eV below it.^{2–4} Energy-resolved scanning tunneling microscopy (STM) was able to connect spectroscopic and structural information:^{5,6} the adatoms of the (7×7) unit cell were identified to cause the S_1 surface state and thus, the finite DOS(E_F), which in turn is responsible for the Fermi level pinning at about 630 meV above the valence band maximum.⁷ This leads to the acceptance of the dimer-adatom stacking fault (DAS) model,^{8,9} which furthermore is confirmed theoretically in several publications.^{10–14}

A finite DOS(E_F) alone, however, does not necessarily mean that the Si(111)-(7×7) surface is metallic. The surface state S_1 responsible for the finite DOS(E_F) is almost dispersionless, in contrast to real metals that are characterized by a dispersive energy band crossing the Fermi energy at $k=k_F$. However, electron energy loss experiments^{4,15,16} (EELS) and the above mentioned STM experiments^{5,6} gave evidence that the Si(111)-(7×7) surface is “truly metallic,”¹⁷ even though no real model based understanding existed. See, in particular, the discussion in Sec. VIII of Ref. 16, which indicates the problems to understand the metallicity of the Si(111)-(7×7) surface on the basis of the ultraviolet photoemission spectroscopy, STM, and EELS experiments, prior to the DAS model and its experimental establishment.

The geometry of the DAS structure model is shown in Figs. 1(a) and 1(b) in the well-known representation by Takayanagi *et al.*^{8,9} displaying the 12 adatoms, 6 rest atoms, and the 9 dimers of the unit cell. Figure 1(c) shows a simplification of the surface reconstruction introduced by Flores *et al.*,^{18,19} assigning the adatoms to two groups: the dimer adatoms and the ring adatoms.

The theoretical work concerning the 7×7 reconstruction of the Si(111) surface addressed in the past mainly questions concerning the reconstruction geometry^{20–23} and the local electronic structure.^{10–14,20,24,25} But until two recent publications that discussed electron correlation effects in the Si(111)7×7 reconstruction^{18,19} only one attempt has been made¹⁶ to understand the effects of the two-dimensional electron gas associated with the adatoms dangling bond (db) states. However, the latter lacks from the fact that it was undertaken just prior to the establishment of the DAS model in 1985.

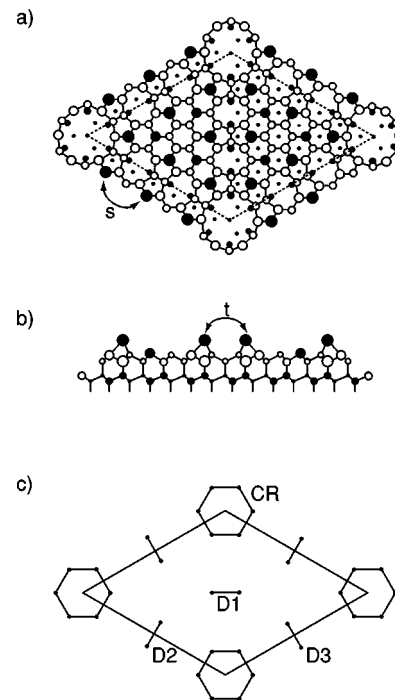


FIG. 1. Geometry of the Si(111)-(7×7) reconstruction: (a) top view, (b) side view. Adatoms are represented by the largest black dots. The hopping integrals t and s between nearest- and next-neighbor adatoms are shown. (c) Scheme showing the corner ring structures (CR) and dimers (D_i , $i=1,2,3$) formed by the adatoms (taken from Ref. 18).

These recent publications on electron correlation effects^{18,19} are based on local density approximation (LDA) calculations of the surface band structure of the Si(111)-(7×7) surface. Models are then constructed to describe the correlation properties of the electrons localized in the surface adatom dangling bonds. The model calculations in both publications result in a highly correlated adatom derived two-dimensional electron gas with correlation times as short as 10^{-14} s for electrons within the central adatom dangling bonds.²⁶ The correlation time associated with the hopping integral in between the central and ring adatom db's is about 3×10^{-14} s. It is this correlation in the two-dimensional adatom electron gas, which finally renders a finite DOS(E_F). Whether such a system, with correlation times by more than an order of magnitude longer than in classical metals can be called “truly metallic” or just a highly correlated two-dimensional electron gas is certainly a matter of taste.

One of the most direct means to learn about the correlation time of an electron gas is the observation of nuclear spin relaxation (nuclear depolarization, spin-lattice relaxation). For a qualitative discussion see in particular Ref. 27, chapter IX and Ref. 28, chapter 5). The fluctuating electron spins generate at a nucleus a fluctuating local field with correlation time τ_c . For correlation times much shorter than the inverse nuclear Larmor frequency ω_L^{-1} (in our case a few MHz) the nuclear spin relaxation (NSR) rate α is proportional to $\tau_c |\overline{H_1^2}|$, the transition probability between nuclear spin sub-states caused by the random perturbation $\hbar H_1(t)$. The bar indicates the time average and α denotes the inverse T_1 time by which a given nuclear polarization decays exponentially. For a Fermi-distributed electron gas the number of electrons that participate in the relaxation process is roughly kT/E_F and thus,

$$\alpha = \frac{1}{T_1} \approx \tau_c |\overline{H_1^2}| \cdot \frac{kT}{E_F}. \quad (1)$$

The NSR rate depends linear on surface temperature and is independent of the strength of an applied external magnetic field.^{27,29,30} (A quantitative expression will be used in Sec. II C).

Application of conventional nuclear magnetic resonance (NMR) techniques to determine T_1 times is hampered for surface science experiments by severe experimental limitations.³¹ Moreover, among the stable Si isotopes only ²⁹Si with an abundance of about 5% carries a magnetic moment. Since at least about 10^{18} equivalent nuclear spins are required for a conventional solid state NMR experiment, which is able to determine relaxation rates, such an experiment is obviously not feasible on a Si(111)-(7×7) surface of typically 1 cm², which carries only about 2×10^{15} ²⁹Si atoms. Moreover, at present no means are known to achieve a surface sensitivity in such experiments. However, using the newly developed particle detected β -NMR method,^{32–34} such measurements are feasible on ⁸Li adsorbed on a Si(111)-(7×7) surface with a Li area density as low as only 10^8 Li atoms per cm². This corresponds to a coverage of about 10^{-7} ML.

Qualitative considerations (large Coulomb repulsion for two electrons in one db) in addition to experimental and theoretical results for alkali metal adsorption on semicon-

ductor surfaces^{35–38} lead to a picture that the Li valence electrons strongly interact with an empty adatom db. Due to its chemical binding the few adsorbed ⁸Li nuclear moments thus watch the fluctuations of the electron gas without changing its overall properties.

Nuclear spin lattice relaxation is only observed if the Li bond to the surface is not completely ionic. This question is raised since the ionicity of the alkali metal atom bond to Si surfaces or of the charge transfer between alkali metal adsorbate and substrate still play a role in the discussion of these systems. It is somehow ill defined, since there is no well-defined measure for these quantities. Part of the recent theoretical investigations characterized the Li bond on the (unreconstructed) Si(111) surface as more ionic than covalent^{39,40} while another⁴¹ finds a more ionic than covalent bond. Because the type of spin-lattice relaxation we are after (Korringa relaxation) relies on the interaction of the ⁸Li nuclear spins with delocalized electrons its observation will definitely exclude a highly ionic bond.

II. EXPERIMENTAL SETUP AND RELAXATION RATES

Most of the tools to perform the experiments have been described in detail elsewhere.^{32–34} Therefore, the technique used is sketched only briefly. It concerns mainly the preparation of the clean Si(111)-(7×7) reconstruction and the hydrogen-covered Si(111) surface, used for comparison, the instrumentation of the ultrahigh vacuum (UHV) chamber, the polarization of the ultrahigh vacuum (UHV) chamber, the polarized ⁸Li atomic beam, and, most important, the *in situ* detection of the nuclear polarization of the adsorbed polarized ⁸Li as function of time. Since NMR techniques are in general not so well known within the surface sciences community we elaborate a bit more than usual on them in what follows.

A. UHV equipment and sample preparation

The UHV-chamber has a base pressure of 5×10^{-11} mbar. Apart from the detection for the β -NMR experiments, the UHV system is equipped with a conventional low energy electron diffraction (LEED) optics (Physical electronics), an Auger-electron spectrometer (Riber), a mass spectrometer (Balzers) for rest gas analysis and temperature programmed desorption spectroscopy, leak valves for gas dosing, and a commercial Kelvin probe (Delta Phi) for work function measurements. Stable Li isotopes can be codeposited from Li getters (SAES Getters).

In order to test the independence of the results from the amount and type of doping a heavily *n*-doped (Sb) sample (about $5 \times 10^{18}/\text{cm}^3$, around the critical density of the nonmetal-metal transition⁴²) and a modest *p*-doped (B) sample (about $10^{15}/\text{cm}^3$) were used. The Si(111) samples (15 mm×12 mm) were cut from two 1.5 mm thick noncommercial wafers [*n*-type (Sb), 0.01 Ωcm , maximum miscut 0.8° and *p*-type (B), 10 Ωcm , maximum miscut $\pm 0.2^\circ$], fully characterized in Ref. 43.

The samples were slotted and mounted on a sample holder comparable to the one described by Bozack *et al.*⁴⁴ Temperature was measured by a tantalum-wrapped NiCr/NiAl thermocouple inserted in a slot at one side of the

sample. Temperature was controlled by a proportional integral differential controller setup on a personal computer to a precision of 10 K.

Prior to insertion into the vacuum chamber the samples were cleaned in an etching process containing the first step to the RCA-clean procedure, using research grade chemicals.⁴⁵ After bakeout, the samples were outgassed several hours at 900 K. Then the oxide was removed by flashes with increasing temperature, finally reaching 1200 K. Hereby the pressure did not exceed 1×10^{-9} mbar. Carbon removal was achieved by Ar^+ -ion sputtering at 500 eV ion energy.

Preparation of the $\text{Si}(111)-(7 \times 7)$ surface thus was performed by Ar^+ sputtering and resistive heating to 1200 K followed by a slow cool-down process passing the “(1 \times 1)” to (7×7) phase transition. The resulting surfaces show O and C contamination at or below the detection limit of our Auger electron spectroscopy-spectrometer. Sharp (7×7) spots are seen in the LEED pattern. During the measurements the surface is cleaned from Li and O every 15 min by flashes to 1200 K.

The hydrogen-covered surface is prepared by adsorbing atomic hydrogen on freshly prepared $\text{Si}(111)-(7 \times 7)$ at a sample temperature of 200 K. The atomic hydrogen is obtained by dissociating molecular hydrogen at a hot tungsten filament ($T=2000$ K) (Refs. 46 and 47) located 3 cm apart from the sample surface. The hydrogen partial pressure was typically 1×10^{-6} mbar. At a hydrogen dose of 150 L (i.e., 150×10^{-6} torr s), hydrogen saturation of the $\text{Si}(111)-(7 \times 7)$ reconstruction was found. This hydrogen dose is used throughout this paper for the preparation of the hydrogen-covered surface.

B. Nuclear polarization

The detection section for electrons from the β decay of nuclear spin polarized ^8Li is connected via a differential pumping section to the source providing a polarized ^8Li atomic beam of thermal velocity. This source, described in detail in Ref. 32 provides a thermal atomic beam of about 10^8 lithium atoms/s, containing a small amount of about 5×10^3 atoms/s of the nuclear spin-polarized radioactive isotope ^8Li . Only ^8Li serves as a probe nucleus for the NMR investigations. Its polarization, to which the detected β -asymmetry is sensitive, is given as the normalized expectation value of the nuclear spin z components

$$P = \frac{\langle I_z \rangle}{I} = \frac{1}{I} \sum_{m=-I}^{m=+I} m \times n_m = n_{+2} + \frac{1}{2}n_{+1} - \frac{1}{2}n_{-1} - n_{-2}. \quad (2)$$

Herein n_m denotes the occupation probability of the z component m of the nuclear spin I of ^8Li ($I=2$). After optically pumping the ^8Li atomic beam, the nuclei are mainly in the $m=2$ state. Typically, the polarization P is about 0.8 to 0.9.

Spin polarization itself is detected via the directional decay asymmetry of the β decay of the ^8Li atom. The asymmetry ϵ of the β -electron intensity with respect to the magnetic field (Fig. 2) is measured through scintillator telescopes and the nuclear polarization of the ensemble is determined through the observation of the asymmetry ϵ

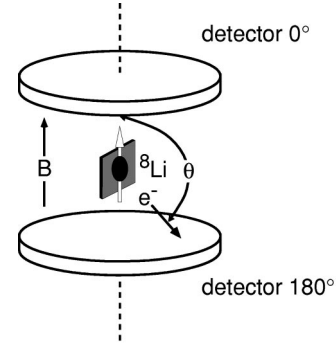


FIG. 2. The principle of β -NMR: The decay electrons are emitted with a higher probability opposite to the direction of the nuclear spin. Therefore, the normalized asymmetry ϵ of the count rate $N(0^\circ)$ and $N(180^\circ)$ yields the polarization of the spin ensemble.

$$\epsilon = \frac{N(0^\circ) - N(180^\circ)}{N(0^\circ) + N(180^\circ)} = -\frac{1}{3}P. \quad (3)$$

$N(0^\circ)$ denotes the count rate for electrons emitted along the direction of the magnetic field, while $N(180^\circ)$ denotes the count rate for electrons emitted opposite to it (Fig. 2). The factor “ $-\frac{1}{3}$ ” is due to the properties of the ^8Li β decay (allowed Gamow-Teller transition⁴⁸). Details of the signal detection can be found in Ref. 34.

C. Nuclear spin relaxation rates

Nuclear spin relaxation (NSR) rates α or their inverse, the T_1 times, describe the exponential decay of the original polarization towards its thermal equilibrium. Even though they are for a spin $I=2$ nucleus in general a sum over up to four exponential decay functions,⁴⁹ within the accessible time domain (see below) it was sufficient to describe the time decay of the asymmetry (nuclear polarization) by one exponential:

$$\epsilon(t) = \epsilon(0)e^{-\alpha t} = \epsilon(0)e^{-t/T_1}. \quad (4)$$

Contrary to conventional NSR experiments (Refs. 27, 29, and 30) the determination of the T_1 time does not require the application of resonant rf fields, since the nuclear spin polarization P in thermal equilibrium (of the order of 10^{-6}) can be neglected compared to the initial polarization of the ^8Li ensemble of 0.8 to 0.9 after deposition.

The NSR experiments consist of two steps (for details see Ref. 33): The production of ^8Li and the accumulation of polarized ^8Li atoms on the surface (activation period typically 0.5 s). The ion beam, as the main source of background signals, is switched off afterwards and the β -electron asymmetry ϵ [Eq. (3)] is detected as function of time over 2 s.

Examples of measured time dependences of NSR rates α are displayed in Fig. 3. In order to receive one set of NSR rate data, the above mentioned cycle has been repeated for 360 times. During the sequence always after ten cycles the direction of the external magnetic field has been inverted. After 80 cycles the surface was cleaned from ^7Li and the adsorbed rest gas by a temperature flash. The flash temperature was close to 1200 K in case of a clean or a Li-dosed surface and close to 400 K for a Si-surface on which H was

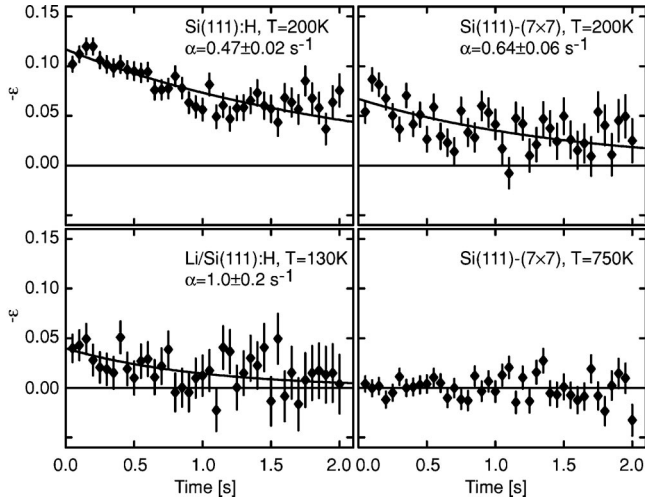


FIG. 3. Nuclear spin relaxation rates as a function of substrate temperature for ^8Li adsorbed on several Si(111) substrates under various conditions and at various temperatures. The average lithium coverage from the atomic beam was below 10^{-7} ML. Only low asymmetries up to about 10% are observed.

adsorbed. Thus, for the H-covered surface the trace amounts of Li were not removed at each cycle.

In the examples displayed in Fig. 3 the decay of the spin polarization with time is shown for varying experimental conditions, together with a fit of an exponential to the spectra. Both, the initial effect $\epsilon(0)$ and the NSR rate α , the latter listed within the plots, depend crucially on surface preparation, on the choice of coadsorbates, and on their coverage. Figure 3(a) shows NSR for lithium adsorbed on a hydrogen-covered Si(111)-(7 \times 7) surface, while Fig. 3(b) displays the decay of polarization under the same conditions, just for the clean sample. The difference observed in the NSR rate α is directly related to the difference in electronic structure of the two substrate surfaces. The coverage of adsorbate atoms also influences the NSR, as demonstrated in Fig. 3(c), where the signal from Li-covered Si(111)-(7 \times 7) surfaces is shown. However, coverage dependent NSR rates will not be discussed within this paper. Figure 3(d) on the other hand shows that the initial polarization is destroyed at 750 K surface temperature so fast that a meaningful determination of NSR rates is not feasible any more.

Since the physics involved in spin-lattice relaxation rates can be either found in text books^{27,29,30,50} or has been discussed extensively for surface experiments elsewhere^{49,51} we give here only a brief sketch of the relation entering the data analysis and its physical content.

As already indicated within the Introduction the main source for electronic NSR in s state dominated highly correlated electrons systems is caused by Fermi contact interaction of the nucleus with fluctuating electronic spins. For Fermi-distributed electrons the necessary mutual spin flip of the nucleus and an electron can only occur for electrons at the Fermi energy. The widely accepted view of this process, which is abbreviated further on as Korringa relaxation, is that a nonequilibrium nuclear magnetization returns to its thermal equilibrium value by a NSR rate $\alpha = 1/T_1$ that is given by

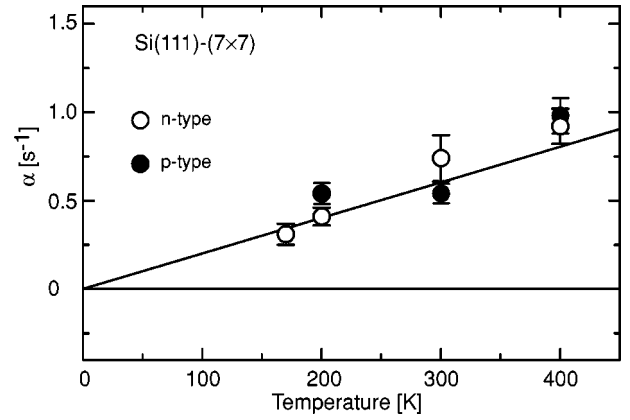


FIG. 4. Nuclear spin relaxation rate α as a function of the substrate temperature for ^8Li adsorbed on a Si(111)-(7 \times 7) surface of samples that were either heavily n or modestly p doped. The average lithium coverage from the atomic beam was below 10^{-7} ML.

$$\alpha = \frac{256\pi^3}{9} \mu_e^2 \left[\frac{\mu(^8\text{Li})}{I} \right]^2 \text{LDOS}(E_F)^2 \frac{kT}{\hbar}. \quad (5)$$

Thus, Korringa relaxation is identified by its linear dependence on the substrate temperature and its independence of the strength of the external magnetic field. Besides the magnetic dipole moments of electron and nucleus, μ_e and $\mu(^8\text{Li})$ respectively, the temperature and the value of the nuclear spin (for ^8Li $I=2$), Eq. (5) contains only the LDOS(E_F) as a variable, which can be determined from measured NSR rates without additional theory. The LDOS(E_F) itself can be factorized

$$\text{LDOS}(E_F) = \langle |\Psi(0)|^2 \rangle \cdot \text{DOS}(E_F) \quad (6)$$

in the DOS(E_F) and the probability $\langle |\Psi(0)|^2 \rangle$ to find an electron at the adsorbed Li nucleus.^{27,29,30} The DOS(E_F) is intimately connected to the correlation times τ_c of the electrons, causing Korringa relaxation [compare Eqs. (5) and (6) with Eq. (1)]. More localized electrons increase the correlation time τ_c . On the other hand, a reduced fraction of active electrons within the unit cell causes the DOS(E_F) to decrease. The resulting DOS(E_F) is therefore always an interplay between these two entities.

III. EXPERIMENTAL DATA

Figure 4 displays $\alpha(T)$ data in between 160 and 500 K for low Li coverage (10^{-5} ML and below) on the clean surfaces of both samples, the heavily doped n -type one and the moderately doped p -type one. 160 K was the lowest achievable surface temperature at the time of the measurement. The NSR rate α increases linearly with temperature, as expected for a correlated electron system that is Fermi distributed, but it does not depend on doping, even though the heavily n -doped sample ($5 \times 10^{18}/\text{cm}^3$) may have already passed the non metal–metal (Mott) transition [critical density for Sb-doped Si (3.0 ± 0.2) $10^{18}/\text{cm}^3$].⁴² This shows clearly that the observed linear increase of the NSR rate does not depend on bulk properties, but it is rather due to a Fermi-distributed

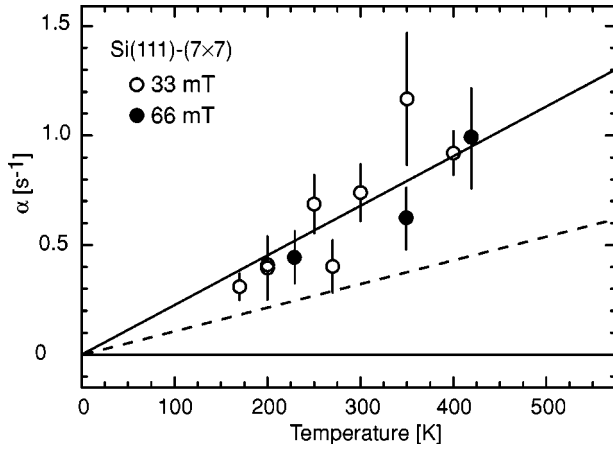


FIG. 5. Nuclear spin relaxation rate α as a function of substrate temperature and two different magnetic fields for ^8Li adsorbed on a clean Si(111)-(7 \times 7) surface. Open symbols indicate an external magnetic-field strength of 33 mT, while full ones a field of 66 mT. The average lithium coverage from the atomic beam was below 10^{-7} ML. The solid line is a fit to the data assuming pure Korringa relaxation [Eq. (5)]. The dashed line indicates the relaxation rates found for low-coverage ^8Li adsorption on a metallic Ru(001) surface from Refs. 49 and 55.

electron gas in the surface. Moreover, relaxation processes due to spin-spin interaction with the Sb nuclear spins can be ruled out. (The two stable Sb isotopes carry both a nuclear spin associated with sizeable nuclear moments.)

Figure 5 displays all the $\alpha(T)$ data collected for the clean 7 \times 7 reconstruction of the Si(111) surface. The error bars are rather large as a consequence of the small initial asymmetry observed for the surface (see Fig. 3). Most of the data are taken at 33 mT as external magnetic-field strength, but doubling it does not change the results within the statistical error bars.

Finally, Fig. 6 shows results for the hydrogen covered surface. The NSR rates are by a factor of 2.5 smaller, but still show as distinct features a linearity in surface temperature and independence of the external magnetic field strength. Furthermore, because of the distinctly different values for the

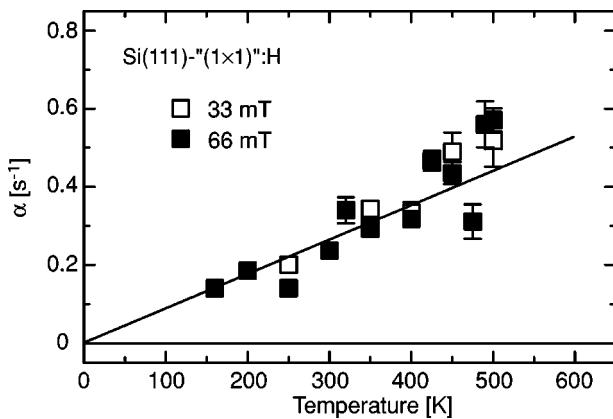


FIG. 6. Nuclear spin relaxation rate α as a function of substrate temperature and two different magnetic fields for ^8Li adsorbed on a hydrogen covered Si(111)-(7 \times 7) surface. Open symbols indicate a strength of the external magnetic field of 33 mT, while full ones a field of 66 mT. The average lithium coverage from the atomic beam was below 10^{-7} ML.

NSR rates observed for the clean and hydrogen covered surfaces the experiment probes features of the sample surface itself and not features of the Li adsorbate. The measurements for the hydrogen covered surface exhibit smaller error bars because of the larger initial effect observed for this surface [see Fig. 3(b)].

On the basis of the experimental results shown in Figs. 4 to 6 it is tempting to interpret the observed linear dependence of the NSR rate α on temperature and its independence on the strength of the magnetic field as caused by Korringa relaxation [Eq. (5)] and therefore the slope of the data in terms of an LDOS(E_F) [Eq. (6)]. From a fit to the data one obtains for the clean surface LDOS(E_F) = $(0.17 \pm 0.01) \text{ eV}^{-1} \text{ \AA}^{-3}$.

This interpretation implies strong evidence that the lithium bond to the Si(111)-(7 \times 7) surface (and hydrogen-covered one) cannot be ionic. If it was purely ionic, the LDOS(E_F) should vanish, since the probability to find an electron at the Li nucleus $\langle |\Psi(0)|^2 \rangle$ vanishes [Eq. (6)]. But just the contrary is observed. Thus, the bond has to be to a large extent ‘‘covalent,’’ irrespective of a quantitative definition of this quantity.

At that point it should be mentioned that for the clean surface in similar experiments performed with ^6Li at much higher sample temperatures as 1000 K a NSR rate of about 4 s^{-1} has been observed,^{52,53} which is twice as large as expected from an extrapolation of the present data to this temperature (Fig. 5). [Relaxation rates for ^6Li and ^8Li are directly comparable since their (μ/I) ratios (γ factors) are accidentally identical within 1%.] New data indicate that this high-relaxation rate is caused by relaxation through diffusion.⁵⁴ Surface diffusion causes moreover at the low magnetic fields used in the present experiment such high relaxation rates at 750 K that it prevents any meaningful determination of them at this temperature [see Fig. 3(d)].

A. Discussion: the Si(111)-(7 \times 7) surface

The observation of Korringa relaxation with its linear dependence on surface temperature T (Fermi distribution of the electrons), its independence of doping and its independence of the external magnetic field strength (rapidly fluctuating electronic spins at the Li nucleus as compared to the Larmor precession time of the nuclear spin in the external magnetic field) points to a highly correlated two-dimensional electron gas on the Li-Si(111)-(7 \times 7) surface at extremely low Li coverages, which is mainly generated by the electrons populating the adatom dangling bonds. This is in accordance with the results of EELS (Refs. 4, 15, and 16) and STM experiments^{5,6} on the clean surface but for the moment hampered by the observation of flat bands of the adatom derived surface state S_1 (corresponding to rather localized electrons) causing the DOS(E_F).³ This, however, might be at least partially a consequence of the large unit cell (small cell in k space).¹³

In addition to the relaxation rate data for the 7 \times 7 reconstruction, Fig. 5 displays as dashed line the relaxation rates found for low-coverage adsorption of ^8Li on Ru(001).^{49,55} At a first glance, it looks very surprising that adsorption of ^8Li on a real metal, with one conduction electron per atomic site, yields a relaxation rate that is by 40% smaller than the one observed for the 7 \times 7 reconstruction of the Si(111) surface.

The relaxation rates of ^8Li on Ru(001) are understood quantitatively in all electron local density calculations for as low coverages as 0.1 ML.^{56,57} They turn out to be about 60% of the ones for Li in Li metal. Their size can, therefore, be considered as typical for Li adsorbed on a metal surface. In the (7×7) reconstruction of the Si(111) surface, however, only in between one¹⁶ to five electrons^{18,19} per unit cell (49 atoms) contribute to the correlated two-dimensional electron gas. One thus expects an about one order of magnitude smaller electron density of states. Even though there is presently no means to conclude that also at E_F the density of states is reduced similarly it would be a big surprise if not. Thus, an enhancement of the relaxation rate of low-coverage ^8Li on Si(111)- (7×7) as compared to a metal (Ru) surface is most probably due to the second term in Eq. (6) or in other terms due to the correlation time τ_c [Eq. (1)]. To be in accordance with the experimental results they have to be at least an order of magnitude larger as compared to metals. Such a trend is, however, not so surprising. In early NMR experiments in semiconductors^{58–60} NSR rates and thus correlation times have been found to be enlarged considerably through the repulsive (Coulomb) interaction of correlated electrons.

The DAS model of the Si(111)- (7×7) reconstruction^{9,8} (Fig. 1) leaves 19 dangling bonds of the originally 49, one of the corner hole atoms, 6 of the rest atoms, and 12 of the adatoms. Experimental and theoretical investigations show that the corner and rest atom db's are energetically located 1 to 2 eV below Fermi level and thus occupied by two electrons,^{5,6,10,11,13,14,18–20,24,25} leaving only five electrons occupying the twelve adatom db's. Two recent theoretical papers analyze the distribution of the five electrons over the 12 adatoms db's on the basis of static LDA calculations and subsequently study correlation effects with a newly formed model Hamiltonian.^{18,19} Figure 1(c) displays the arrangement of the 12 adatoms in the (7×7) unit cell of the DAS model, together with those from adjacent cells. Closest to one another are the electrons of dangling bonds in the "ring" around the corner hole and within the "dimers." A calculation of the ground state energy shows as most favorable configuration the one with three electrons in the ring and two electrons distributed over the three adatom dimers of a unit cell formed from the central adatoms. Within this model it is the threefold degeneracy of this configuration that finally creates the correlated two-dimensional electron gas (metallicity of the surface). Thus, within this model there are in lowest order two electrons per unit cell moving along the different dimers and rings, which make up the surface metallicity. This has to be compared with about one electron per unit cell estimated from the width of the elastic scattering peak in an EELS experiment.¹⁶

The hopping integrals amount to $t\approx 75$ meV for hopping within the ring or within one adatom dimer, but only to $s\approx 25$ meV for hopping between two dimers or the ring and a dimer or vice versa.^{18,19} The main effect of the hopping integral s is to connect the threefold degenerate ground state configuration thus lifting the degeneracy and allowing two electrons per unit cell to move along the adatom dimers. From the detailed model calculation a band around E_F with a width of about 100 meV appears.

Hopping integrals of only 25 or 75 meV lead to correlation times τ_c of about 3 or 1 times 10^{-14} s, up to 10 times longer than for classical metals, but still within the "metallic" regime.⁶¹ But anyhow, this time is still much smaller than the Larmor precession time of the nuclear spin of the probe nuclei $1/\omega_L\approx 2\times 10^{-7}$ s in the external magnetic field. It is thus not in conflict with the independence of NSR rates from the strength of the external magnetic field.

The adsorption of alkali metals is always accompanied by a strong reduction in sample work function, which is explained at least for low coverage with a strong charge transfer from the alkali metal to the substrate surface. This charge transfer can only proceed through adsorption at the adatom site, since the corner and rest atom sites are already occupied and cannot take up the extra charge from the Li atom. Thus, at low enough coverage the valence electron of the adsorbed ^8Li interacts strongly with an empty adatom db. At the extremely low coverage at which the experiments have been performed (10^{-5} ML and below) only a very minor fraction of electrons is added to the correlated two-dimensional electron gas of the clean surface without influencing its properties. We thus believe that as compared to a metal (Ru) surface the enhanced measured NSR rates directly reflect the enlarged correlation times of the two-dimensional electron gas of the bare 7×7 reconstruction of the Si(111) surface.

At present no quantitative relationship between the measured LDOS(E_F) at the Li nucleus and the electronic structure of the clean Si(111)- (7×7) exists. Because of the large unit cell all electron calculations for low-coverage adsorption of Li on the Si(111)- (7×7) surface are not feasible. To reduce the size of the unit cell we presently study the LDOS (E_F) at the Li nucleus as a function of Li coverage on the hydrogen-terminated Si(111)- (1×1) :H surface. In this way, the unit cell will be reduced considerably and hopefully model calculations, following the spirit of the ones for the bare surface would^{18,19} become feasible on this highly perfect semiconductor surface.

B. Discussion: the Si(111)- (1×1) -H surface

The significance of the LDOS(E_F) for NSR rates may perhaps be tested by using a hydrogen saturated Si(111)- (7×7) surface.^{46,62,63} Even though this surface is not to be mistaken for the highly perfect Si(111)- (1×1) :H-terminated surface, prepared by wet-chemical preparation, it is characterized by a largely reduced density of states at the Fermi level.^{64,65} It, however, shows a large density of various defect structures.⁶⁶ In particular, one finds still isolated adatoms and small islands that are made up of the missing adatoms from the exposed regions of the rest layer (cf. Fig. 4 or Ref. 66). Moreover, also top layer atoms with a missing hydrogen are observed.^{62,63}

Nevertheless, in the present experiments relatively large relaxation rates (Fig. 6), which are only by a factor of about 2.5 smaller than for the clean surface (Fig. 5), have been observed. Despite the claimed vanishing DOS(E_F) they show all properties of Korringa relaxation: linearity in surface temperature T and magnetic field independence.

In any case the finite and magnetic field-independent relaxation rate points towards electronic relaxation with fluctuations much faster than the Larmor frequency. Whenever it was checked quadrupolar relaxation turned out to be by orders of magnitude too small to account for the observed re-

laxation rates. Thus, the simplest but rather unlikely solution to explain the observed data would assume a still existing but extremely small $\text{DOS}(E_F)$ not visible in UPS experiments. It might be compensated in the observed $\text{LDOS}(E_F)$ [Eq. (6)] by a still further enhanced correlation time τ_c for the fluctuating electrons interacting with the ^8Li nuclear spin as compared to the clean (7×7) surface.

A certainly more promising way to analyze the data is to assume that the surface is really semiconducting and the fluctuating electrons in the valence band obey a Boltzmann distribution. Then for completely ionized donors (number of conduction electrons independent of T) the relaxation rate will be proportional to $T^{1/2}$ (for a derivation see Chap. IX, III of Ref. 27). For the other extreme, a free electron gas in thermal equilibrium the number of electrons in the valence band is proportional to $T^{3/2}$ (see Chap. 28 of Ref. 61) and the relaxation rates becomes proportional to T^2 . Certainly all intermediate powers will appear, also the one around 1. At the moment a more detailed analysis is asked for. However, prior to such one the donors at the hydrogen covered Si(111) surface, their amount and their properties have to be identified.

A final possibility that comes into one's mind rather naturally thinking of the imperfection of the hydrogen covered surface is nuclear spin relaxation through coupling to paramagnetic centers (unpaired electronic spins) generated by structural defects. For a detailed discussion of this mechanism see Chap. IX of Ref. 27. Aside from a strength factor including average distances to the sixth power, the moments and spins squared, and numerical factors the relaxation rate is proportional to

$$\alpha \propto \frac{2\tau_e}{1 + (\tau_e \cdot \omega_L)^2}. \quad (7)$$

ω_L denotes the Larmor frequency, which depends on the strength of the external magnetic field and τ_e denotes the correlation time for spin fluctuations of the nearby paramagnetic centers. Magnetic field independence is achieved if $\omega_L \tau_e \ll 1$, that is $\tau_e \ll \omega_L^{-1} \approx 10^{-7}$. If so, however, α would be proportional to τ_e , which governs now the temperature dependence. In order to describe the trend of the experimental data well, the electronic correlation time has then to increase with temperature. This is in strong disagreement with all experience from electron spin resonance experiments (see, e.g., Refs. 67 and 68 and references therein).

IV. OUTLOOK

In general, NSR rates are always proportional to the typical correlation time τ_e . In Eqs. (5) and (6) this dependence is hidden within the probability to find the electron at the probe nucleus. Following recent theoretical considerations,^{18,19} which are in accordance with experimental findings,¹⁶ only

two electrons per (7×7) unit cell contribute to the DOS (E_F), causing its strong reduction as compared to metal surfaces, where about one electron per surface atom contributes to its metallicity. The large $\text{LDOS}(E_F)$ at the Li nucleus adsorbed on the (7×7) reconstructed Si(111) surface is therefore most likely caused by an interplay of an enlarged probability to find a delocalized electron at the adsorbed Li nucleus (longer correlation times as in classical metals) and a reduced $\text{DOS}(E_F)$ of the Si(111)- (7×7) surface itself. The rather long correlation times found in a theoretical analysis of the electronic structure of the surface^{18,19} are supported by our NSR experiments.

This picture may perhaps be valid also for the surprisingly observed finite $\text{LDOS}(E_F)$ at the Li atoms adsorbed on the hydrogen covered surface. An extremely small $\text{DOS}(E_F)$, not observable in UPS experiments might be compensated in the observed $\text{LDOS}(E_F)$ [Eq. (6)] by a still further enhanced correlation time τ_c and thus the probability to find a still weakly delocalized electron at the adsorbed Li nucleus.

To obtain a detailed understanding, a quantitative comparison of theoretical predictions and our results is called for. Meanwhile, all electron calculations of the $\text{LDOS}(E_F)$ for Li adsorbed at various coverages on a metal (Ru) surface are available.^{56,57} It has to be seen in the future whether computer facilities are capable enough for codes treating the problem of low coverage adsorption of Li on Si(111)- (7×7) .

Such calculations should also treat the adsorption site of Li on the reconstructed (7×7) surface. NMR experiments sensitive to the static electric field gradient (EFG) at the nucleus indicate that it is positive for Li adsorption on the (7×7) surface.⁵³ Adsorption of Li on closed packed metal surfaces (W, Mo, and Ir) leads to negative EFG's.⁶⁹ This is interpreted as an adsorption on top of the surface atoms. It is, therefore, very unlikely that Li adsorbs on top of an adatom, since that would lead to a negative EFG.⁵² Only adsorption in between the two Si adatoms of an adatom dimer or of two adatoms of a ring (see Fig. 1) might lead to a positive EFG, if the geometry is such, that Si atoms and the adsorbed Li atoms are roughly within a plane perpendicular to the surface normal.

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