Nuclear Magnetic Resonance Studies of Chemisorption of Alkali-Metal Atoms on a W(110) Surface

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NMR measurements were performed with nuclear-spin–polarized alkali-metal atoms (^{6}Li, ^{7}Li, ^{23}Na) adsorbed on a clean and an oxygen-covered W(110) surface. For the desorbed alkali-metal ions the change of polarization due to the radio-frequency field was detected by beam-foil spectroscopy. Energy splittings of the nuclear states were found arising from the interaction of nuclear quadrupole moments with electric field gradients. They reflect the spatial charge distribution in the vicinity of the adsorbed alkali-metal atoms.

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The interaction of atoms and molecules with solid surfaces has been of general interest for many years. Although a variety of experimental methods has been developed, there is nevertheless a lack of methods which directly probe spatial charge distributions of surfaces and adsorbed atoms. The electronic charge distribution is of particular interest. It is, for example, the basic quantity of one of the most important theoretical methods used for the calculation of surface properties and chemisorption processes, namely the density-functional theory.[1,2] Such calculations require a detailed experimental check.

In solids, liquids, and chemical systems, NMR studies turned out to be one of the most powerful techniques for obtaining such microscopic information. However, the application of these methods to solid surfaces is limited,[3] primarily for the following reasons. Conventional NMR measurements, which are based on the very small nuclear polarization governed by the Boltzmann distribution for the nuclear m substates, need a considerable number of probe nuclei. These are not available for systems which are most interesting in surface physics studies, i.e., single-crystal surfaces with a low adsorbate coverage. Moreover, it is in general difficult to distinguish between the bulk and the surface signal.[4]

We have developed a NMR technique for which these two difficulties do not arise. This will be demonstrated for alkali-metal atoms (Li, Na) adsorbed on a clean and an oxygen-covered W(110) surface. The principle of our method is as follows (Fig. 1). A thermal alkali-metal atom beam is nuclear-spin polarized by use of a sextupole magnet and a subsequent adiabatic radio-frequency transition,[5] which determines the initial nuclear-spin polarization of the atomic beam. The fact that the probe atoms are prepared in a source means that the polarization is large. Because we do not utilize the Boltzmann distribution for the nuclear m substates, we need neither low temperatures nor high magnetic fields at the surface. The thermal nuclear-spin–polarized alkali-metal atom beam impinges on the surface to be investigated which is kept at temperatures of 1000 to 1500 K in ultrahigh vacuum. The sample is mounted between two coils which produce the rf field. The surface coverage with alkali-metal atoms was in all cases less than 10^{-3} of a monolayer. The alkali-metal atoms get desorbed from the surface partly as neutral atoms, partly as positive ions. Only the positive ions are used for detecting nuclear-spin polarization by beam-foil spectroscopy.[6] In what follows we do not describe the beam by the occupation probabilities N_m of the nuclear m substates but rather by the components of a polarization tensor t_{k0}. The first component t_{10}, which is the only one used for the demonstration of this NMR method, is proportional to the expectation value of the magnetic moment of the beam and therefore also called vector polarization. It is related to the N_m values by $t_{10} = (\frac{3}{2})^{1/2}(N_1 - N_{-1})$ for spin $I = 1$ (^{6}Li) and by

$$t_{10} = (\tfrac{9}{5})^{1/2}[(N_{3/2} - N_{-3/2}) + (N_{1/2} - N_{-1/2})/3]$$

for $I = \frac{3}{2}$ (^{7}Li, ^{23}Na).

Compared to free alkali-metal atoms the charge distribution in the vicinity of the nuclei of the adsorbed atoms no longer has spherical symmetry.

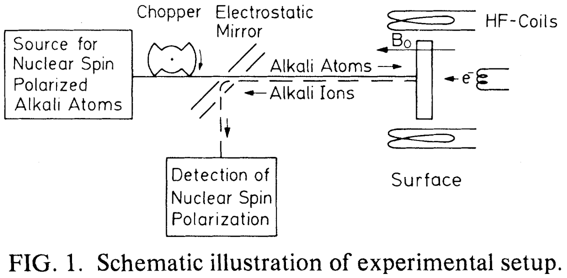

FIG. 1. Schematic illustration of experimental setup.

Therefore the redistributed charge of the alkali-metal atoms and the surface electrons produce an electric field gradient (EFG) which interacts with the nuclear quadrupole moment (Q). This is the most important interaction we observe in the present experiment of alkali-metal adsorption on a transition metal.

At temperatures of 1000 to 1500 K the mean residence time of the alkali-metal atoms on the surface is about 1 to 10^{-4} s. During this time the nuclear moments of these atoms interact with the EFG generated by the spatial charge distribution in their vicinity, with the external static magnetic field, and with the rf field. At these temperatures, of course, the EFG is randomly fluctuating as a result of surface diffusion of adsorbed alkali-metal atoms. Their jumping rate Γ determines the correlation time τ_c of the fluctuations ($\tau_c = 1/\Gamma$). Analogous to the mean residence time, it obeys an Arrhenius equation with an activation energy for diffusion of about 0.5 to 0.7 eV. At 1300 K τ_c is of the order of 10^{-10} s. This time has to be compared with the Larmor frequency $\omega_{\rm L}$ of the nuclear magnetic moments in the external static magnetic field ($B_0 \sim 0.01$ to 0.1 T). For the isotopes ^{6}Li, ^{7}Li, and ^{23}Na $\omega_{\rm L}$ is about 0.1 to 10 MHz. The fluctuations of the EFG are very fast compared to $\omega_{\rm L}$ ($\tau_c << 1/\omega_{\rm L}$). This means that in the NMR experiments we always measure an averaged EFG (motional narrowing[7]). Nevertheless the fluctuating part of the EFG causes a relaxation of the nuclear polarization.[5] In order to minimize this depolarization we have to choose a suitable temperature, so that the mean residence time is sufficiently short.

The Hamiltonian of the static interaction on the surface consists of a dipolar part H_D and a quadrupolar part H_Q. H_D is due to the interaction of the magnetic moment with the external magnetic field and results in an equidistant Zeeman splitting of the states. The Hamiltonian of the quadrupolar interaction depends on the orientation of the EFG tensor relative to the external magnetic field B_0. Assuming that the largest principle axis of the EFG tensor V_{zz} coincides with B_0, we get the Hamiltonian[7,8]

$$H_Q = eQV_{zz}\frac{3I_z^2 - I^2 + \frac{1}{2}\eta(I_+^2 + I_-^2)}{4I(2I-1)}, \tag{1}$$

where $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter of the EFG tensor.

The equidistant Zeeman splitting of the states results in one single resonance line at the Larmor frequency $\omega_{\rm L}$. The additional quadrupolar interaction leads to a splitting of this resonance line into two lines for a spin $I = 1$ system (^{6}Li) or into three lines for an $I = \frac{3}{2}$ system (^{7}Li, ^{23}Na). For an EFG with rotational symmetry ($\eta = 0$) the two lines for $I = 1$ occur at the frequencies $\omega_- = \omega_{\rm L} - 3\omega_Q$ and $\omega_+ = \omega_L + 3\omega_Q$ with $\omega_Q = eQV_{zz}/4\hbar$. Three lines occur for $I = \frac{3}{2}$ at $\omega_- = \omega_{\rm L} - 6\omega_Q$, $\omega_{\rm L}$, and $\omega_+ = \omega_{\rm L} + 6\omega_Q$ with $\omega_Q = eQV_{zz}/12\hbar$ [Eq. (1)]. If there is no longer a rotational symmetry or if the principal axis of the EFG is tilted with respect to B_0 there can also be a shift of the middle line with respect to $\omega_{\rm L}$ ($I = \frac{3}{2}$) and a different deviation of the upper and lower lines from $\omega_{\rm L}$ ($\omega_+ - \omega_L \neq \omega_{\rm L} - \omega_-$).

As an example Fig. 2 displays two NMR spectra of ^{6}Li adsorbed on an oxygen-covered W(110) surface. As expected for a spin $I = 1$ nucleus interacting with a static magnetic field B_0 and an EFG, both spectra show two lines. According to Eq. (1) the splitting of about 720 Hz corresponds to an EFG component $V_{zz} = 3.08(8) \times 10^{15}$ V/cm^2. The two spectra differ from each other by the way the incident atomic beam was prepared (see inset in Fig. 2). Displayed in the lower part is a measurement with a preparation for which one transition ($m = 1$ to $m = 0$) causes an increase of the polarization, while the other one ($m = 0$ to $m = -1$) causes a decrease. From the sequence of these transitions it is possible to determine the sign of the EFG component V_{zz}.

Figure 3 displays two NMR spectra for ^{23}Na, on a clean and an oxygen-covered W(110) surface. In agreement with Eq. (1) for a spin $I = \frac{3}{2}$ system the

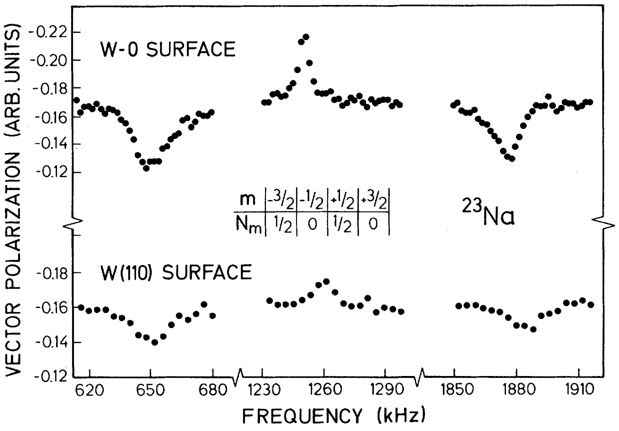

FIG. 2. NMR spectra of ^{6}Li on an oxygen-covered W(110) surface with two different preparations of the atomic beam. The Larmor frequency $\omega_{\rm L}/2\pi$ is 102.1(1) kHz.

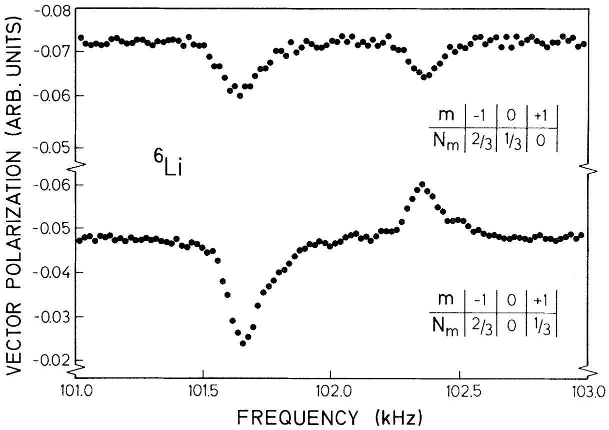

FIG. 3. NMR spectra of ^{23}Na on a clean and an oxygen-covered W(110) surface. For both experiments the Larmor frequency $\omega_L/2\pi$ is 1257.4(10) kHz.

spectra show three resonance lines. According to the preparation of the beam (see inset to Fig. 3) the middle line (transition from $m = +\frac{1}{2}$ to $m = -\frac{1}{2}$) shows an increase of polarization. Since the relaxation rate on a clean surface is larger than that on the oxygen-covered one, we had to choose a shorter mean residence time (higher temperature). Consequently the lines in the spectra we got on the clean surface are less saturated. In contrast to the experiment using ^{6}Li, the quadrupolar splitting for ^{23}Na ($6\omega_Q/2\pi \simeq 600$ kHz) is in the same order of magnitude as the Larmor frequency ($\omega_L/2\pi \simeq 1260$ kHz). Therefore the off-diagonal part of the Hamiltonian [Eq. (1)] affects the spectra and results in a nonequidistant splitting. Consequently the asymmetry parameter η can be determined from these spectra.[9] The sign of V_{zz} was deduced from experiments similar to that for ^{6}Li as described above. The values of the EFG for ^{6}Li, ^{7}Li, and ^{23}Na on the clean and oxygen-covered surfaces are shown in Table I.

The EFG component V_{zz} for ^{23}Na is always negative and its magnitude is not much affected by the oxygen coadsorption. In contrast to this the EFG seen by the Li isotopes is also negative for the clean W(110) surface but positive for an oxygen-covered surface. Moreover, $|V_{zz}|$ for Li is more than one order of magnitude smaller than that for ^{23}Na. This difference is partly due to the response of core electrons to the external EFG. This can approximately be accounted for by the Sternheimer antishielding factors for the free alkali-metal ions.[11] It is about 5 for Na and 0.8 for Li. This means that the EFG is amplified by the core electrons in the case of Na but is attenuated for the Li nucleus. Nevertheless there is a remaining difference between the EFG's of Na and Li.

TABLE I. Experimental values of the EFG components V_{zz} and asymmetry parameter η.

Nucleus	Q (mb)[a]	T (K)	B_0 (T)	V_{zz} (10^{15} V/cm^2)	η
			W(110)		
^{6}Li	-0.7	1130	0.0163	0.0(4)	...
^{7}Li	-37	1210	0.0479	$-1.1(1)$	...
^{23}Na	$+110$	1290	0.1116	$-47.4(3)$	0.07(1)
			W-O		
^{6}Li	-0.7	1160	0.0163	$+3.08(8)$	...
^{7}Li	-37	1265	0.0479	$+2.59(2)$	...
^{23}Na	$+110$	1245	0.1116	$-46.8(1)$	0.02(1)

[a] Ref. 10.

The components of the EFG at the position of the nucleus are given by the electronic charge distribution ρ folded with spherical harmonics Y_{2q} of rank 2. For example V_{zz} is given by

$$V_{zz} = \int r^{-3}(3\cos^2\theta - 1)\rho(r,\theta,\phi)\,d^3r, \tag{2}$$

where θ denotes the angle to the normal of the surface plane (z axis) and ϕ the angle in the x-z plane. The component V_{zz} therefore is negative if the electron charge is more concentrated along the z axis, and positive if it is located more in the x-y plane. Of course at finite temperatures the adsorbed atoms are not at rest but vibrating parallel and perpendicular to the surface. Therefore by measuring the EFG we are measuring the averaged charge distribution.

For the electron transfer from the alkali atom to the surface we can expect that V_{zz} is negative if the adsorbed atom is further away from the surface and that it is positive if it is more or less embedded in the surface. In this way we can understand two trends of V_{zz}. First, the sodium atom is larger than the lithium atom, and consequently it is further away from the surface. Therefore, V_{zz} for ^{23}Na should be more negative than that for the Li isotopes. Secondly, we can assume that the atom-to-metal separation increases on average with increasing temperature. The ^{7}Li measurements were performed at higher temperatures (larger relaxation rate) than those for ^{6}Li and its EFG component V_{zz} is smaller (more negative). This behavior was also confirmed for ^{23}Na by experiments not discussed here.

The asymmetry parameter η reflects the deviation of the EFG and consequently of the charge distribution from a rotational symmetry around the normal to the surface plane. The W(110) surface has a twofold symmetry. Therefore we can expect a nonvanishing value of η as confirmed by the experiment (Table I). On the oxygen-covered W(110) surface the value of η is much smaller. Obviously the structure of the W(110) surface is washed out more or less by the oxygen overlayer. This may be because the experiments were performed at an oxygen partial pressure of 10^{-6} mbar. The coverage therefore need not correspond exactly to a monolayer of oxygen.

Unfortunately, it is not possible at the moment to compare our results with theoretical predictions. Although calculations concerning alkali-metal adsorption on tungsten already exist,[12,13] the authors did not extract an EFG, probably because they did not know that it is measurable.

The method presented here, namely, NMR studies by application of highly nuclear-spin–polarized probe atoms and detection of polarization with high efficiency, is not restricted to the use of alkali-metal atoms on transition-metal surfaces. It has been shown[14] that on semiconductor surfaces the ionization process also works with high efficiency. Moreover, experiments are in progress to detect the nuclear polarization of neutral atoms by laser excitation of hyperfine levels.[15] If this method of detection turns out to be successful, the investigation can be extended to a wide range of surface material and probe atoms. Another promising variation of this method is the use of polarized radioactive atoms adsorbed on surfaces. In this case, for example, the NMR signal can be taken to be the asymmetry of the β decay.

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