

# Nuclear Quadrupole Interaction of Alkali-Metal Atoms Adsorbed on Metal Surfaces \* . \*\*

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A new technique is discussed for probing microscopic details of surface charge distributions using beams of thermal-velocity nuclear-spin-polarized atoms. The technique has made possible one of the first spin-relaxation and the first nuclear-spin-resonance experiments on single-crystal metal surfaces.

The investigation of nuclear quadrupole interaction in solids by nuclear methods has a long standing tradition [1]. Nuclear-spin-polarized probes have provided detailed microscopic information on charged distributions in the environment of the probing atom. Nuclear magnetic resonance (NMR), nuclear level mixing (NLM) and nuclear spin relaxation (NSR) experiments are typical applications of what is now widely known as “nuclear solid-state physics”. Its transfer to solid surfaces is aggravated generally by two severe problems: on one side on a surface the number of probing nuclear moments is extremely small as compared to the number generally available in a solid, on the other side in general an exclusive surface sensitivity is hard to achieve. In recent years we developed a method [2–5] which overcame these problems at least for alkali-metal atoms adsorbed on hot metal surfaces mainly of high work function. NMR, NLM and NSR experiments were performed and delivered first microscopic information on the electronic structure of alkali-metal atoms bound to metal surfaces. The charge distribution in the vicinity of the adsorbed alkali-metal nuclei no longer has the spherical symmetry of the free atom. Therefore, the redistributed charge of the alkali-metal atoms and the nearby surface electrons produces an electric field gradient (EFG) which interacts with the nuclear

quadrupole moment  $Q$ . This is the primary effect observed in the present experiments with alkali-metal atoms adsorbed on transition metal surfaces.

The principal features of our nuclear surface physics experiments are illustrated in Figure 1. A thermal-velocity, nuclear-spin-polarized atomic beam impinges on the sample surface, which is kept at temperatures of 1000 to 1500 K in UHV. The sample is situated in a static magnetic field  $B_0$  which defines the quantization axis for the system. A pair of coils mounted near the surface supplies the rf-field needed in NMR-experiments. The surface coverage by the alkali-metal atoms in the experiment reported here was always less than  $10^{-3}$  of a monolayer. This allows to neglect mutual interaction of the adsorbates. The alkali-metal atoms desorb thermally from the surface partly as neutral atoms, partly as positive ions. Up to present, the nuclear polarization of the ions is measured via beam-foil spectroscopy [6].

At temperatures of 1000–1500 K the mean residence time of alkali-metal atoms on the surface to be investigated is from 1 to  $10^{-4}$  s. During this time, the nuclear moments of these atoms interact with

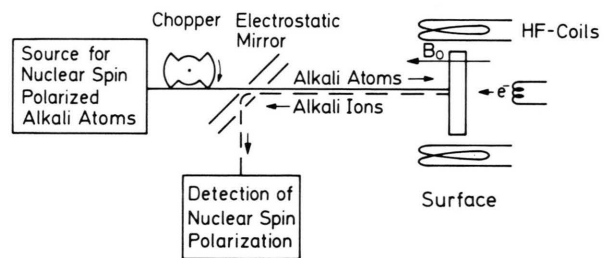


Fig. 1. Schematic view of the apparatus used in the nuclear surface-physics experiments.

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the EFG generated by the spatial charge distribution in their vicinity, with the external static magnetic field and with the applied rf-field. The EFG is randomly fluctuating as the result of surface diffusion of the adsorbed alkali-metal atoms. The jumping rate of this adsorbates  $\Gamma$  determines the correlation time  $\tau_c$  of the fluctuations ( $\Gamma = 1/\tau_c$ ). At the above temperatures  $1/\tau_c$  is of the order of  $10^{10} \text{ s}^{-1}$ , much larger than the Larmor frequency  $\omega_L$  of the nuclear magnetic moments in the external static magnetic field.

With  $\tau_c \ll 1/\omega_L$ , the fluctuations of the EFG are rapid compared to time constants characteristic of the nuclear polarization, so that we are always in the “motional narrowing” regime, and hence measure an average EFG [7]. Nevertheless, the fluctuating part of the EFG causes NSR constraining the choice of surface temperatures (i.e., mean residence time) in order to minimize this depolarization. By lack of space NSR-experiments cannot be discussed here further.

The Hamiltonian  $H$  of the static interaction on the surface consists of a dipolar part  $H_D$  (interaction of rank 1) and a quadrupolar part  $H_Q$  (interaction of rank 2).  $H_D$  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 principal axis of the EFG tensor  $V_{zz}$  coincides with  $B_0$ , we obtain the Hamiltonian [1, 7]

$$H = H_D + H_Q = \mu B_0 \frac{I_z}{I} + e Q V_{zz} \frac{3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)}{4I(2I-1)},$$

where  $\eta = (V_{xx} - V_{yy})/V_{zz}$  is the asymmetry parameter of the EFG tensor. In an NMR experiment the equidistant Zeeman splitting of the states results in one single resonance line at the Larmor frequency  $\omega_L$ . The additional quadrupolar interaction leads to a splitting of this resonance into  $2I$  lines the frequency distance of which is directly proportional to the EFG  $V_{zz}$ .

We shall describe the polarization of the beam either in terms of occupation numbers  $N_m$  of the nuclear magnetic substates or in terms of the so-called vector polarization  $t_{10}$ , which for a spin-1

particle such as  ${}^6\text{Li}$  is related to the occupation numbers  $N_m$  by  $t_{10} = \sqrt{(3/2)} (N_{+1} - N_{-1})$ .

Figure 2 displays as an example NMR spectra of  ${}^6\text{Li}$  adsorbed on an oxygen-covered W(110) surface (W-0) each showing the expected two resonance lines for a spin-1 nucleus interacting with a static field  $B_0$  and an EFG. The measured splitting in the upper curve of about 720 Hz corresponds to an EFG component  $V_{zz} = 3.08 \times 10^{15} \text{ V/cm}^2$ . The difference between the upper and lower spectra arises from the differing preparations of the incident atomic beam. In the lower spectrum of Fig. 2 rf-transitions between the  $m = 1$  to  $m = 0$  substates cause an increase of the polarization, while the transition from  $m = 0$  to  $m = -1$  causes a decrease. The order of these transitions as a function of frequency determines the sign of  $V_{zz}$  (positive). Similar experiments have been performed for  ${}^7\text{Li}$  and  ${}^{23}\text{Na}$  on a W-0 surface and for these three alkali-metal isotopes on a clean W(110) surface [4].

From NLM experiments [5] information is gained similar to that obtained from NMR studies. We shall discuss the method and the results obtained with nuclear-spin-polarized  ${}^{23}\text{Na}$  chemisorbed on a W-0 and W(110) surface. The experimental arrangement is the same as described above. The nucleus  ${}^{23}\text{Na}$  has spin  $I = 3/2$  and its vector polarization is given by

$$t_{10} = \sqrt{(9/5)} \{ (N_{3/2} - N_{-3/2}) + (N_{1/2} - N_{-1/2})/3 \}$$

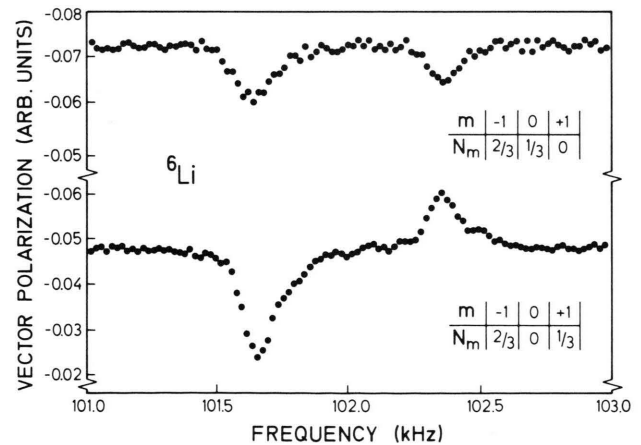


Fig. 2. NMR spectra of  ${}^6\text{Li}$  on an oxygen-covered W(110) surface with two preparations of the atomic beam. The Larmor frequency  $\omega_L/2\hbar$  is 102.1(1) kHz. The insets refer to the relative  $m$ -substate populations  $N_m$  of the incident beam.

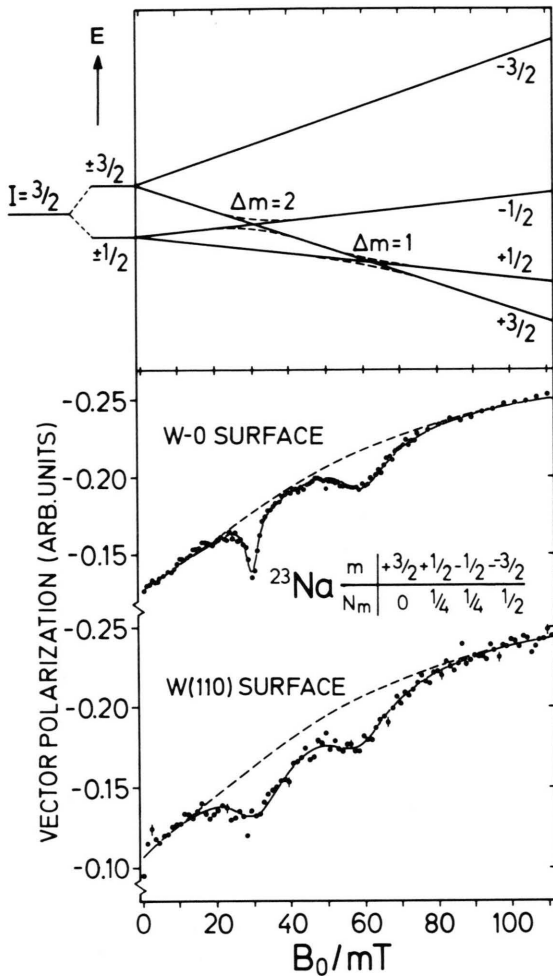


Fig. 3. *Upper part:* Zeeman effect for an  $I = 3/2$  nucleus in the presence of an electric field gradient. *Lower part:* Vector polarisation of  $^{23}\text{Na}$  ions desorbing from a clean and from an oxygen-covered W(110) surface as a function of external magnetic field strength. The relative magnetic substate occupation numbers  $N_m$  for the incident beam are shown in the inset.

The level scheme for an  $I = 3/2$  nucleus interacting with a magnetic field is displayed in the upper part of Figure 3. For  $B_0 = 0$  one observes the quadrupole splitting. The degeneracy of the  $m = \pm 3/2$  and  $m = \pm 1/2$  levels is removed by the Zeeman splitting for  $B_0 > 0$ . At the crossings, the degeneracy of the levels will be resolved and they will mix if the Hamiltonian is no longer axially symmetric. Mixing of levels with  $\Delta m = \pm 2$  arises if the EFG tensor is not axially symmetric anymore ( $\eta \neq 0$ ). Mixing of

levels with  $\Delta m = \pm 1$  arises when the surface normal is tilted with respect to the external magnetic field defining the  $z$ -axis of the system. In the present experiment this angle was chosen to be  $5.2^\circ$ . The dashed lines in the upper part of Fig. 3 display qualitatively the removal of the degeneracy of the levels at the crossing points. The size of the mixing ratio (shape of the resonances) for a given magnetic field strength  $B_0$  is a measure of this strength of the non-axial part of  $H$  (the asymmetry parameter and the tilting angle). The magnetic field at which the crossings occur determines the axial part  $V_{zz}$  of the EFG tensor.

The lower part of Fig. 3 displays the vector polarization of  $^{23}\text{Na}$  ions desorbing from a W-0 and a W(110) surface as a function of the external magnetic field. In addition to the two pronounced "resonances" at  $B_0 \cong 30$  mT and at  $B_0 \cong 60$  mT a smooth increase of polarization as a function of the external magnetic field strength can be observed. This effect arises from the mixing of atomic levels due to the hyperfine interaction and changes the nuclear polarization as the beam approaches the surface region with its external magnetic field.

For both surfaces, the "resonances" occur at the same magnetic field strength, indicating that  $V_{zz}$  is the same for both surfaces. Since for both surfaces the tilt angle was the same ( $5.2^\circ$ ), the higher field resonances should also appear identical, as in fact they do. However, the pronounced differences in shape of the two lower-field resonances indicate that the asymmetry parameter of the EFG tensor must be quite different in the two cases. A fit to the data yields  $\eta = 0.12$  and  $0.48$  for W-0 and a W(110) surface, respectively.

The results obtained in both experiments (NMR and NLM) are summarized in Table 1. For  $^{23}\text{Na}$  the EFG component  $V_{zz}$  is always negative and its magnitude is not much affected by the coadsorbed oxygen. In contrast, the EFG seen by the Li isotopes is negative for the W(110) surface but positive for the W-0 surface. Moreover,  $V_{zz}$  for Li is over an order magnitude smaller than that for  $^{23}\text{Na}$ . This is partly due to the response of core electrons to the external EFG, and maybe approximately accounted for by the Sternheimer antishielding factors for the free alkali ions [8]. It is about 5 for Na and 0.48 for Li. Even taking this into account, however, there remains a real difference between the EFG's experienced by Na and Li.

Table 1. Measured values of EFG component  $V_{zz}$  and asymmetry parameter  $\eta$ .

Surface	Nucleus	Method	$T$ (K)	$B_0$ (mT)	$V_{zz}$ ( $V/cm^2$ ) $\times 10^{15}$	$\eta$
W (110)	$^6\text{Li}$	NMR	1130	16.3	0.0(4)	—
	$^7\text{Li}$	NMR	1210	47.9	− 1.1(1)	—
	$^{23}\text{Na}$	NMR	1290	111.6	− 47.4(3)	0.42(6)
	$^{23}\text{Na}$	NLM	1360	—	− 49.0(4)	0.48(12)
W-0	$^6\text{Li}$	NMR	1160	16.3	+ 3.08(8)	—
	$^7\text{Li}$	NMR	1265	47.9	+ 2.59(2)	—
	$^{23}\text{Na}$	NMR	1245	111.6	− 46.8(1)	0.12(6)
	$^{23}\text{Na}$	NLM	1360	—	− 49.8(1)	0.12(6)

There exists presently no real microscopic calculation of EFG's for chemisorbed atoms taking into account the structure of the surface in detail. There exists a schematic model [9] which assumes that the valence electron of the chemisorbed Na atom alone generates the EFG. It is assumed that this electron is shared by the four neighbouring W-atoms of a W(110) surface, and localized with an amplitude of one-fourth the full charge density at half the distance between the Na atom and the four neighbouring W atoms. This model overestimates the EFG component  $V_{zz}$  by approximately a factor of 4. However, since the symmetry of the surface is taken into account, the asymmetry parameter  $\eta$  turns out to be different from 0 and to have the right magnitude.

Comparison can also be made with results of an ambitious cluster model calculation [10] which treats Na chemisorbed on a W(100) surface (four-fold symmetry) rather than a W(110) surface (two-fold symmetry). Therefore,  $\eta$  is identically zero in this calculation. Moreover, since the calculation assumes a spherically symmetric electron distribution for each individual atom in a Wigner-Seitz cell, it is not surprising that it underestimates the measured value of  $V_{zz}$  by as much as a factor 4.

Last not least there exist now first theoretical results for EFG's at the nucleus of alkali atoms adsorbed on jellium [11]. These calculations really intend to receive first insight into the physics of the present experiment. The model by definition yields  $\eta \equiv 0$ . It predicts the correct sign of the observed EFG and a reasonable order of magnitude of its size

for Li and Na. Whereas it yields for Li an almost vanishing EFG, which is a result from a cancellation of contributions to the EFG from the bare (jellium) metal electrons and the rest (atom) it underpredicts for  $^{23}\text{Na}$  the EFG by a factor of 2. In these calculations temperature dependencies of the EFG were found to be rather small.

The experimental results and their discussion display clearly that NMR and NLM experiments are feasible in surface physics on a much wider scale than expected previously. Certainly the feature of the present method to be restricted to atoms which low ionization energy adsorbed on hot metal surfaces of high work function is a severe limitation of the experiments described. Therefore, presently experiments are underway, in which the nuclear polarization of the desorbing atoms (not ions!) are to be measured by laser induced fluorescence. The results [12] are very encouraging and will allow experiments in which different crystal surfaces with different work functions can be compared. But still up to now the ions or atoms have to desorb from the surface in order that their nuclear polarization can be determined. This requires a high temperature of the surface. One might get rid of this if radioactive nuclei are used. For  $\beta$ -asymmetry measurements presently a test experiment which uses  $^8\text{Li}$  is in advance [13]. If it is successful such experiments are opened to the full temperature range. Moreover, there will be no restriction whatsoever to systems with certain ionisation energies and work functions.

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