

Magnetic Hyperfine Fields at Se Adatoms on Ni Surfaces

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Magnetic hyperfine fields for Se on Ni(111) and Ni(001) surfaces were measured with the perturbed angular correlation technique. The results are $|B_{\text{hf}}| = 2.7(3)$ T for Se on Ni(111) and $|B_{\text{hf}}| = 0.8(3)$ T for Se on Ni(001) at 90 K. These values of magnetic hyperfine fields of an *adatom* deviate drastically from the known bulk value of $B_{\text{hf}} = 15$ T. The surface site positions of the probe atoms are discussed with the aid of the results for the electric hyperfine interactions measured simultaneously. [S0031-9007(96)01654-7]

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During the past decades numerous measurements of magnetic hyperfine fields (B_{hf}) at impurities have been performed in the bulk ferromagnetic $3d$ elements Fe, Co, and Ni [1,2]. In the beginning of the eighties, two theoretical approaches yielded rather reliable results for most of the elements in the different series of the periodic table [3,4]. Thus, the electronic structures responsible for the magnetic hyperfine fields are essentially calculable. Considerable deviations from the bulk values might occur, when the impurities are located close to or at the surface or at an interface. To date, only a few experiments have been published with probe atoms positioned in atomic layers close to or at the surface [5] or at an interface [5,6]. Most of these experiments were carried out with the ^{57}Fe Mössbauer probe, where Fe layers are involved, or with the ^{111}Cd perturbed angular correlation (PAC) probe nucleus, where Cd, as an isolated impurity, was used to study ferromagnetic systems. So far, no experiment has been published where B_{hf} at the nuclei of *adatoms* on a ferromagnetic surface has been determined. This is due to experimental obstacles. For the ferromagnetic $3d$ elements, Fe ($T_C = 94$ K) and Co ($T_C = 1404$ K) with very high Curie temperatures, T_C , diffusion, and even desorption of adatoms from surfaces would prevent measurements for the larger part of the ferromagnetic temperature range. Ni ($T_C = 630$ K) offers the opportunity for stable adatom positions even above T_C for strongly bound elements. The changes of the magnetic properties of the Ni surfaces due to the presence of adsorbates have been the subject of numerous experimental, as well as theoretical, studies [7]. Here, we present an investigation of the magnetic influence on the *isolated adatom* itself.

On low-Miller-index surfaces, such as Ni(001) and Ni(111), adsorption sites of halogens and chalcogens have been studied quite intensively, e.g., of Cl [8,9], of Br [10], and Se [11]. The radioactive isotope ^{77}Br , decaying to ^{77}Se with a recoil energy of 3.9 eV [12], is known

to be a suitable PAC probe [2]. In PAC experiments with $^{77}\text{Br}/^{77}\text{Se}$ probes, adsorption, site occupation on the surface, and desorption reflect the properties of the parent Br, while the hyperfine interactions are measured at the daughter ^{77}Se . Our measurements with ^{77}Br were performed with coverages as low as 10^{-3} of a monolayer (ML). These extremely low concentrations consequently must be compared to the lowest coverages of the earlier studies [8–10].

The present experiment was performed in the UHV chamber ASPIC (Apparatus for Surface Physics and Interfaces at CERN) at the UHV beam line of the on-line mass separator ISOLDE at the BOOSTER facility [13]. The mass separator provided beams of radioactive ^{77}Rb ions which were implanted at an energy of 60 keV into a precleaned molybdenum foil in the catcher chamber (base pressure of 5×10^{-8} Pa) of ASPIC. Several hours later, after the implanted ^{77}Rb ($T_{1/2} = 3.9$ min) had decayed via ^{77}Kr ($T_{1/2} = 75$ min) to ^{77}Br inside the Mo foil, the Br atoms were evaporated onto the surface of a second precleaned molybdenum foil by resistance heating of the catcher foil. The second foil was transferred by a manipulator into the main chamber of ASPIC (base pressure 2×10^{-9} Pa). Here, the Br atoms were evaporated onto the prepared surface of the sample mounted on an x - y - z - ϕ manipulator equipped with cooling (LN_2) and heating devices (up to 700 K).

Single crystals of Ni (and Pd for comparative measurements) as disks of 13 mm diameter and 1 mm thickness with (001) and (111) surfaces [14] were prepared by argon sputtering and annealing at 1000 K. The surface structure and purity were controlled *in situ* by low-energy electron diffraction and Auger-electron spectroscopy. Reproducible PAC results were obtained for overall surface contamination (mainly C,P,S) of less than 3% of a ML.

The γ - γ cascade (755 and 250 keV) of the electron capture decay product ^{77}Se has an unusually high

anisotropy coefficient of $A_{22} = -0.454$. The relevant properties of the isomeric intermediate nuclear state are spin $I = 5/2$, half live $T_{1/2} = 9.3$ ns, nuclear g factor $g_N = +0.447(10)$ [15], nuclear electric quadrupole moment $|Q_N| = 0.76(8)$ b [16]. In the time-differential PAC experiment, combined interaction frequencies $\omega_c = \omega_c$ (ω_Q, ω_L) are observed, which depend on the Larmor frequency of the magnetic hyperfine interaction $\omega_L = g_N \mu_N B_{\text{hf}}/\hbar$ (μ_N nuclear magneton, no external field was applied) and the electric quadrupole interaction frequency $\omega_Q = eQ_N V_{zz}/4I(2I - 1)\hbar$ [V_{zz} electric field gradient (EFG)] arising from the (strongly) noncubic environment of the adatoms.

For the comparative measurements on Pd surfaces, only quadrupole interactions are present. With a four-detector array the ratio of the count rates C eliminates the nuclear half-life

$$R(t) = [C(180^\circ) - C(90^\circ)]/[C(180^\circ) + C(90^\circ)]. \quad (1)$$

Here, the angles between the detectors are given in degrees.

A selection of PAC time spectra is shown in Fig. 1. The experimental data in the form of Eq. (1) are fitted to the general expression describing the perturbed angular correlation for static electric and magnetic interactions on single crystals. The parameters are calculated numerically [17]. The results derived from the parameters ω_Q , ω_L , and $A_{22\text{eff}}$ are collected in Table I. All spectra could be fitted assuming only one site of the probe atoms for each surface. Different sites would reveal themselves in different interaction frequencies as has been shown in several earlier studies [18]. From $A_{22\text{eff}}$ we derive that 60%–90% of the ^{77}Br ions occupy a unique site. The rest might be located at surface imperfections or contaminations. We first regard the results for the EFGs in order to discuss the surface site occupation. The temperature dependence of the V_{zz} values is shown in Fig. 2(a). For Se on Pd(001), we found the highest absolute value of V_{zz} of all surfaces investigated. A linear temperature dependence yields the best fit to the data. With this result the assumption is justified that the Br ions keep the position they have obtained when evaporated onto a Pd(001) surface at 90 or 300 K, at least up to 560 K. The V_{zz} values of Se on Ni(001) could be measured without additional magnetic interaction above the Curie temperature at about 650 K. Evaluating the magnetic and electric interaction frequencies for measurements below T_C , we found the same temperature behavior of the EFG on Ni(001) as on Pd(001). The EFG of Se on Pd(111) was determined at room temperature, and on the Ni(111) surface it was extracted from the combined interaction frequencies. When raising the temperature of the Ni(111) sample above 400 K, the PAC time spectra could no longer be fitted with the assumption of only a single fraction, probably caused by mobility on the surface starting at this temperature. Summarizing the essential results on the EFGs, we would like to note

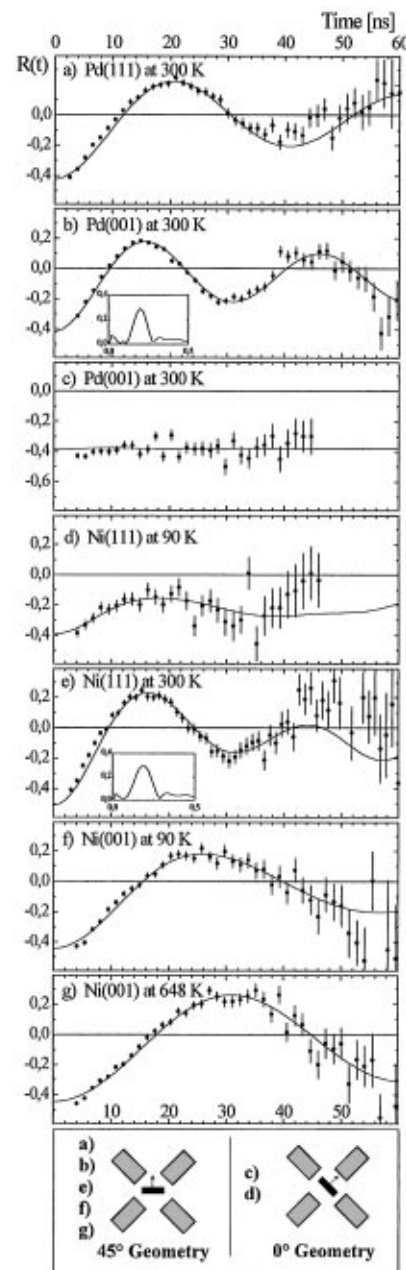


FIG. 1. PAC time spectra [see Eq. (1)] for ^{77}Se adatoms on (a) Pd(111), (b) Pd(001), (e) Ni(111), (f,g) Ni(001) surfaces at different temperatures. The respective detector geometries are shown below. In (c) and (d) only the 180° spectra of the detectors perpendicular to the crystal surface against one of the 90° spectra were taken. The solid lines represent fits to the data [17]. Exemplarily, in (b) and (e), Fourier transforms are inserted.

that (i) we present the first measurement of an EFG of an adatom over a wide temperature range; earlier measurements were only possible in the low temperature range [19]. (ii) The absolute value of the EFG on Pd is stronger for the (001) surface than for the (111) surface and vice versa for Ni. (iii) EFGs in bulk materials usually show a $T^{1.5}$ dependence [20], whereas it has been proposed that

TABLE I. Results of the PAC measurements.

Crystal surface	T [K]	ν_Q^a [MHz]	$ B_{\text{hf}} ^b$ [T]	Fraction ^c [%]
Pd(001)	90	111(5)	--	62(8)
	295	107(3)	--	68(5)
	563	101(3)	--	60(7)
Pd(111)	295	81(2)	--	74(4)
	90	62(2)	1.3(3)	75(6)
Ni(001)	295	59(2)	0.8(3)	73(6)
	295	60(2)	1.0(2)	71(4)
	648	55(2)	0	74(4)
	658	54(2)	0	70(4)
	90	91(2)	2.8(2)	88(4)
Ni(111)	295	99(2)	2.3(3)	91(5)

$$^a\nu_Q = 4I(2I - 1)\omega_Q/2\pi.$$

^bDerived from ω_L .

^cEffective A_{22} coefficient ($A_{22\text{eff}}$) from fit to Eq. (1) divided by nuclear A_{22} coefficient [15].

two-dimensional systems tend to exhibit a linear temperature dependence [21].

We now turn to discuss the B_{hf} results. As can be seen in Fig. 1, the electric quadrupole interaction dominates the PAC time spectra for the experiments on Ni, i.e., only very small B_{hf} s are present. In spite of the short half-life, the extraction of B_{hf} is possible because of the extraordinarily large A_{22} coefficient. A more “visible” effect is obtained, when the surface normal of the single crystal sample (which is parallel to the direction of the EFG axis) is turned into one detector direction (0° geometry in Fig. 1). For Pd(001), as expected for the nonmagnetic case, no perturbation of the angular correlation is observed, and a constant $R(t) = -0.4$ results [Fig. 1(c)]. For Ni(111), the angular correlation is perturbed even in this geometry as a direct consequence of the magnetic field involved, Fig. 1(d). The direction of the B_{hf} at the Se atom was found to be in plane for Se on Ni(001) and to be tilted by $35(10)^\circ$ for Se on Ni(111). This has to be investigated closer in experiments with externally applied fields.

In Fig. 2(b) the results are plotted together with the temperature dependence of the bulk magnetization of Ni normalized to the surface measurements at 90 K (dashed and dotted lines). The most striking observation is the drastic drop from the value of +15 T for Se in bulk Ni [2] to the fields of $\approx|3|$ T for Se on Ni(111) and of $\approx|1|$ T on Ni(001). Regarding the B_{hf} s of the $4sp$ elements in Ni as shown in Fig. 3, selenium occupies the maximum in the series. As Kanamori, Yoshida, and Terakura concluded from their calculations [3], the positive fields originate from the antibonding interaction with the majority spin electrons. Dederichs *et al.* [4] confirmed this interpretation using a Green’s function approach. The results of both calculations are included

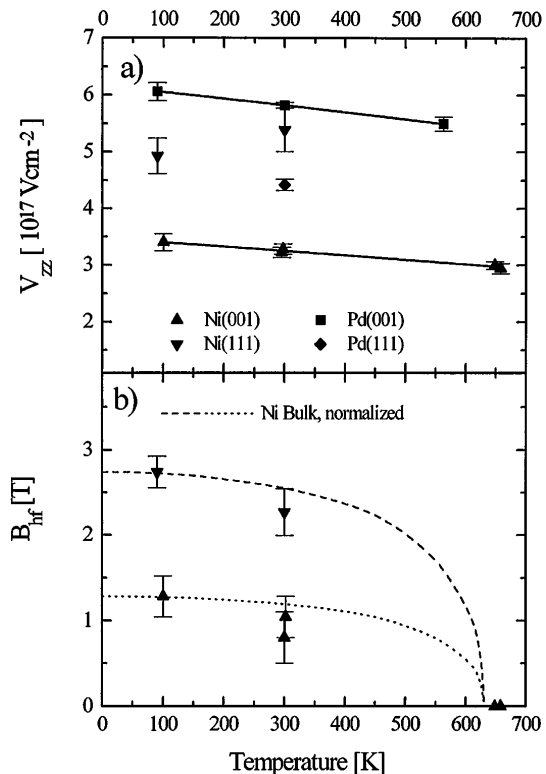


FIG. 2. Electric field gradients (V_{zz}) in (a) for Se on Ni and Pd (001) and (111) surfaces, and magnetic hyperfine fields (B_{hf}) in (b) for Se on Ni (001) and (111) surfaces. Solid lines in (a) are fits to a linear temperature dependence. Dashed and dotted lines in (b) show the bulk magnetization of Ni according to Weiss and Forrer [22], normalized to our measurements at the lowest temperature of 90 K.

in Fig. 3. The strong deviation of the surface values from the bulk field yields a significant reason for a future theoretical treatment of this problem. Theory has focused increasing interest on surface magnetism and recently on magnetic properties of adsorbates and also adatoms [23]. It is well known [7] that the chalcogens O and S as adsorbates even at fractions of a ML coverage change the surface electronic structure with the result of a considerable reduction of the magnetic moment at the Ni surface. Our measurements for the chalcogen Se yield the local magnetic response at the isolated impurity. Fortunately, in the present case, the most important properties for a theoretical treatment are known: The surface sites are the fourfold hollow site on Ni(001) and the fcc threefold hollow site on Ni(111) [8–10] with known structural parameters for the perpendicular spacing between the adatoms and top substrate layers [11]. No site change is expected during the decay of (monovalent) ^{77}Br to (divalent) ^{77}Se , since earlier investigations have shown that the sites occupied by Br are also stable for Se [11] in the low adsorbate concentration range. Calculations may find out whether the Se impurities lead to a drastic reduction of the magnetic polarization of the

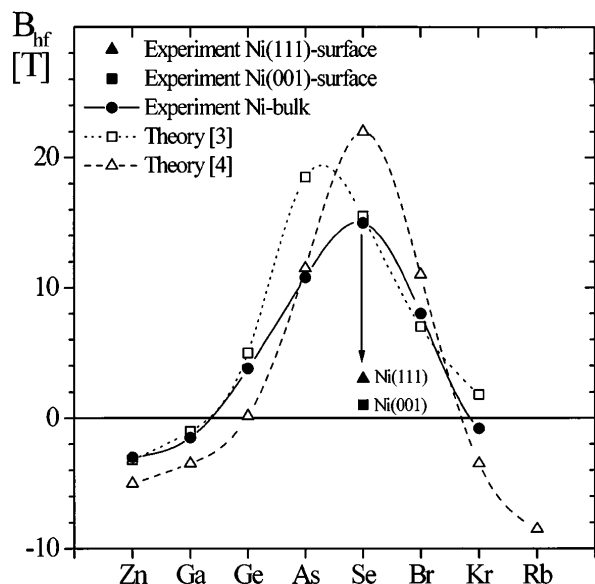


FIG. 3. Magnetic hyperfine fields in Ni for the elements Zn, ..., Rb. Solid line: experimental data from Refs. [1,2,24]. Dotted line: bulk, theory of Kanamori *et al.* [3]. Dashed line: bulk, theory of Dederichs *et al.* [4]. The sign of the B_{hf} values for the Se adatoms (\blacksquare , \blacktriangle , present work) was not determined.

topmost Ni atoms or if the different contributions to the magnetic hyperfine field cancel accidentally.

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