Monolayer-Resolved Detection of Magnetic Hyperfine Fields at Cu/Ni(111) Interfaces

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The magnetic behavior of the bordering Ni and Cu monolayers at the interface of ultrathin Cu films on Ni(111) has been investigated. ^{111}In probes have been used, utilizing perturbed $\gamma\gamma$ angular correlations, to study strength, orientation, and temperature dependence of the magnetic hyperfine field at the probe nuclear site. This magnetic hyperfine field is strongly reduced to about 50% in the first Ni layer covered by Cu; it vanishes in the adjacent Cu layer. The results are compared to hyperfine fields at free Ni(111) surfaces, to magnetometry measurements, and to theoretical predictions.

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The magnetic properties of ferromagnets covered by nonmagnetic materials and the magnetic polarization of these coverages has become a matter of considerable interest in both experiment and theory. The magnetic interaction is generally present only over a short range at the interface between magnetic and nonmagnetic materials. Therefore, detailed investigations require experimental methods with monolayer resolution. Interfaces buried below very thin overlayers can be studied by spin- and element-sensitive surface methods[1] like spin-resolved Auger electron or photoelectron spectroscopy. However, if the interface is covered by a thicker film, only hyperfine techniques can be utilized.

So far, only Mössbauer spectroscopy at ^{57}Fe probe atoms has been used to study interface magnetism with monolayer resolution. The magnetic hyperfine field $B_{\rm hf}$ at Fe(110) surfaces is increased by Ag coverage.[2] Similarly, the interfaces of 4-monolayer (ML) Fe films sandwiched in Au show enlarged hyperfine fields as compared to the central layers.[3]

The perturbed $\gamma\gamma$ angular correlation (PAC) technique, which—like Mössbauer spectroscopy—is based on the hyperfine interaction of probe nuclei with extranuclear electromagnetic fields, has a high potential for surface[4] and interface[5] studies. There are certain aspects which make the PAC method extremely favorable as a complementary approach to study interface magnetism with monolayer resolution. In this Letter we shall report on the first application of PAC to magnetism at interfaces.

In contrast to the Mössbauer experiments performed so far, where about 1 ML of ^{57}Fe probes is needed, in PAC the concentration of probes is reduced by orders of magnitude to about 10^{-4} ML. This, on the other hand, makes it possible to study individual monolayers at surfaces, interfaces, and thin films of many materials, since they can be labeled with radioactive PAC probes acting as isolated observers. In addition, the superior sensitivity of PAC to structural information via the electric-field gradient permits the determination of probe sites.[6]

For the present PAC experiments we utilize the isomeric nuclear state ($I=\frac{5}{2}$, $t_{1/2}=84$ ns) of the 171-245-keV $\gamma\gamma$ cascade in ^{111}Cd, which is populated by electron capture of ^{111}In ($t_{1/2}=2.8$ d). The detection of γ_1 selects a subgroup of states within the isomeric nuclear level, resulting in an anisotropic γ_2 emission in delayed coincidence with respect to the detection of γ_1. The interaction of the nuclear magnetic dipole moment [$\mu=-0.7656(25)\mu_N$] and the nuclear electric quadrupole moment [$Q=0.83(13)$ b] of the isomeric state with hyperfine fields splits this nuclear level, causing a time dependence of the $\gamma\gamma$ angular correlation. This time dependence is characterized by frequencies ω_n, which are the transition frequencies between the nuclear sublevels. In the presence of only a magnetic hyperfine field at ^{111}Cd the Larmor frequency and its first harmonic appear; in the case of a pure electric-field gradient three transition frequencies occur and for a combined interaction up to fifteen transition frequencies may occur.[7] With a five-γ-detector setup we record simultaneously sixteen coincidence spectra from which eight different counting-rate ratios $R(t)$ are extracted.[8] These $R(t)$ spectra can be expressed as a superposition of cosine and sine modulations with the frequencies ω_n. Fourier analyses of the $R(t)$ spectra directly exhibit the transition frequencies; the set of hyperfine parameters, however, is extracted by a least-squares fit applied simultaneously to the full set of time-dependent counting-rate ratios. From this procedure the strength and direction of $B_{\rm hf}$ as well as the strength (V_{zz}), symmetry, and principal-axis orientation of the electric-field-gradient tensor are obtained.

Sample preparation and PAC experiments were carried out in an ultrahigh-vacuum system with a base pressure of 3×10^{-9} Pa. Disks cut from a [111]-oriented Ni single crystal were cleaned in ultrahigh vacuum by cycles of Ar^+ sputtering and subsequent annealing up to 1250 K. The crystallographic structure of the surface was monitored by low-energy-electron diffraction (LEED); the chemical purity was checked by Auger electron spectroscopy (AES). The resulting total impurity concentration was below 2% ML. Subsequently, radioactive ^{111}In

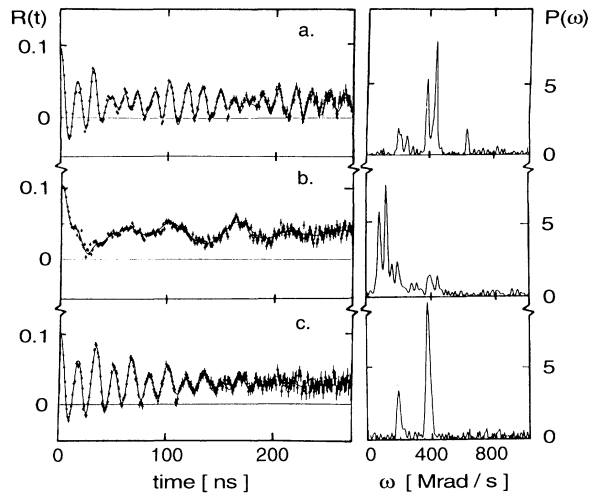

FIG. 1. PAC spectra and corresponding Fourier transforms (a) for ^{111}In(^{111}Cd) probe atoms in the topmost monolayer of Ni(111) surfaces, (b) after covering with about 1.6 ML of Cu at substrate temperature of 200 K, and (c) for probe atoms at the topmost monolayer of a 1.6-ML Cu film on the Ni(111) substrate.

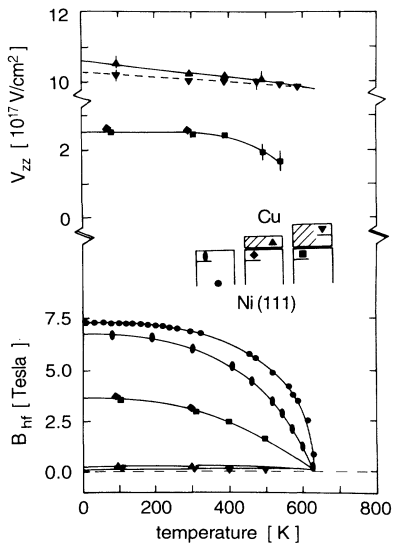

FIG. 2. Temperature dependences of the electric-field gradient V_{zz} and the magnetic hyperfine field B_{hf}. The different symbols represent the ^{111}In(^{111}Cd) probe atoms at various positions in the Cu/Ni(111) system (see inset).

probe atoms were deposited onto the Ni surface with a concentration of about 10^{-4} ML. Finally, the samples were annealed to 850 K for 10 min.

PAC experiments for the ^{111}In-labeled free Ni(111) surface have been reported earlier.[6] They indicate that the probe atoms occupy substitutional terrace sites in the topmost monolayer of the Ni(111) surface. A typical PAC spectrum for this situation is shown in Fig. 1(a). B_{hf} is found to be reduced over the entire temperature range as can be seen in Fig. 2 (lower part).

In order to study the influence of a thin Cu coverage on the magnetism of the Ni surface layer, a few ML of Cu were evaporated onto the Ni surface at a rate of 0.05 ML/s. The substrate temperature was chosen to be either 200 or 300 K. The LEED pattern showed sharp spots revealing epitaxial growth. The measurement of the 920-eV Cu-*LMM* Auger electron intensity as a function of film thickness indicates layer-by-layer growth of the ultrathin Cu films.

The evaporation of a few ML of Cu onto the ^{111}In-labeled Ni(111) surface leads to a drastic change in the strength of the hyperfine fields. Figure 1(b) shows that the PAC frequencies that occur are now smaller. Both magnetic and electric hyperfine fields are present at the probes. Their quantities and their temperature dependence are shown in Fig. 2. A small axially symmetric electric-field gradient (Table I) oriented perpendicular to the interface plane is detected and indicates that the probes still occupy their initial lattice sites in the first Ni monolayer, where the field gradient results from the broken charge symmetry at the Cu/Ni interface. In case the ^{111}In probes had segregated to the Cu surface

TABLE I. Magnetic-hyperfine-field parameters and electric-field gradient for ^{111}In(^{111}Cd) probes in different Ni systems.

	In Ni bulk	At free Ni(111) surface	At Ni(111) surface covered with Cu	At surface of 1 ML Cu on Ni(111)	At surface of 2 ML Cu on Ni(111)
$B_{hf}(T=0\ \mathrm{K})$ (T)	7.2(1)	6.65(9)	3.6(1)	<0.26 [a]	<0.08 [a]
b ($10^{-8}\ \mathrm{K}^{-5/2}$) [b]	4.21(1)	8.2(9)	9.4(10)	...	...
$V_{zz}(T=0\ \mathrm{K})$ [c] (10^{17} V/cm^2)	0.0	11.4(3)	2.6(3)	10.6(3)	10.3(3)

[a] B_{hf} at 77 K.
[b] $B_{hf}(T)=B_{hf}(T=0\ \mathrm{K})(1-bT^{5/2})$.
[c] Error of nuclear quadrupole moment not included.

different hyperfine frequencies would be observed [see below, Fig. 1(c)]. The strong difference in the hyperfine parameters reveals that possible surface segregation of ^{111}In probes is easily detectable and can be excluded in Fig. 1(b).

After establishing the ^{111}In probe sites, we now want to discuss the magnetic properties of the interface. B_{hf} is reduced remarkably to about 50% of the bulk value (see Fig. 2). Above 400 K, B_{hf} is oriented in the plane, and it tilts out by 5.5(10)° at 100 K, a behavior similar to that of the uncovered surface.[4] Since no external magnetic field was applied, no preferred in-plane direction can be expected. Most likely, B_{hf} points along equivalent [110] directions in the (111) plane which are the second easy axes of magnetization in Ni bulk. The easy magnetization axes point along [111], which are not existent in the (111) interface plane.

The temperature dependence of B_{hf} at ^{111}In(^{111}Cd) probes in Ni bulk, in the topmost monolayer of low-index single-crystal Ni surfaces,[9] and in the Cu-covered Ni(111) surface layer is well represented by the function $B_{hf}(T)=B_{hf}(T=0)(1-bT^{5/2})$ between 80 and 400 K. A $T^{3/2}$ contribution, as expected from spin-wave theory, is quite small in this temperature interval. Measurements below 80 K have only been performed for ^{111}In probes in Ni bulk,[9] and in this temperature range a $T^{3/2}$ term contributes significantly to the temperature dependence of B_{hf}. For Ni bulk, B_{hf} at ^{111}In(^{111}Cd) probes essentially scales with the spontaneous magnetization.[10]

Table I shows that the temperature dependence of B_{hf} at the interface to the nonferromagnetic copper behaves like the one for the uncovered surface. In either case, the parameter b is enlarged compared to the bulk value due to the lack of ferromagnetic-coupled nearest neighbors. A similar trend was found for Ag-covered Fe(110) surfaces and thin films of Fe.[2]

Now we turn to the magnetic behavior of the Cu film. For that purpose 1, 1.6, and 2 ML of Cu were evaporated onto the Ni single crystal as described before; afterwards the probe atoms were deposited. The resulting impurity concentration was again below 2% ML.

As can be seen in Fig. 1(c), the PAC measurements show a strong electric-field gradient (Table I) with axial symmetry and an orientation perpendicular to the surface plane. The temperature dependence is displayed in Fig. 2. This proves that the probes occupy substitutional terrace sites in the topmost monolayer of the Cu films.[6] The strengths of the field gradients are nearly independent of the Cu film thickness and are similar to those found for the uncovered Cu(111) surface.[6]

The magnetic hyperfine field B_{hf} nearly vanishes even at low temperatures in the Cu films (see Fig. 2, lower part). From the broadening of the transition frequencies at 77 K we deduce upper-limit values of 0.26 and 0.08 T for the 1- and 2-ML Cu films, respectively. However, this broadening may also be due to the lower structural order of the films compared to well-prepared single-crystal surfaces. All of these results are summarized in Table I.

The reduction of B_{hf} for ^{111}In(^{111}Cd) probes at the Ni(111) surface compared to those in Ni bulk is mainly due to the reduced number of neighboring ferromagnetic moments. This leads to a reduced polarization of the 5s valence electrons at our probe atoms ^{111}Cd, which via the Fermi-contact interaction cause the magnetic hyperfine field at the probe nuclei. As for Cd in Ni bulk the polarization of the Cd core electrons is expected to be negligible.[11] In addition, a reduction is also expected by a changed conduction-electron density at the surface due to Friedel oscillations, resulting in a reduced Fermi-contact field. This has been predicted for Ni(100) and Fe(110) surfaces.[12]

Covering the surface with another conducting material reduces the Friedel oscillations and thus B_{hf} should slightly increase. This was experimentally found for Ag and Au overlayers on Fe(110) surfaces.[2,3] Our Ni case is in contrast to this finding; the covering of the Ni surface with Cu leads to a drastic reduction of B_{hf}.

This effect can be explained by the electronic interaction of the Cu overlayers with the ferromagnetic Ni 3d states, which for the analogous case of Ag and Au overlayers on Fe does not exist. Indeed, slab calculations[13-15] reveal several possible mechanisms leading to a decrease of the magnetic moments at the interface: a hybridization of Cu sp with Ni d states, an interatomic charge transfer from sp to d states, and a broadening of the d states at the Ni interface monolayer. The calculations yield the largest reduction of the magnetic moment at the Ni interface monolayer, whereas in the second Ni layer almost bulklike behavior is expected. Moreover, even for 1 ML of Cu, almost the band structure of Cu bulk is found, without any considerable magnetic polarization. Our results are in good agreement with these findings.

Magnetometry measurements for thick Ni films covered with Cu show a decrease of the total magnetic moment of the sample,[16] the loss being equivalent to 58% of the magnetic moment of 1 ML of Ni in bulk. Our results show that B_{hf} at the interface is reduced by 46% compared to the uncovered surface. The magnitude of B_{hf} for ^{111}In in Ni is expected to scale roughly with the magnetic moments of the nearest-neighbor atoms.[10,12] Considering that Friedel oscillations at the surface are stronger than at the interface, the reduction of the magnetic moments deduced from B_{hf} should even be larger than 46%. Comparing our results with that of magnetometry measurements, we therefore conclude that most of the total reduction of the magnetic moment takes place only in the first interface Ni monolayer, whereas both the Cu interface monolayer and the second Ni layer behave almost like bulk material.

In conclusion, we have demonstrated that PAC experi-

ments yield information on the magnetism of interfaces with monolayer resolution. The monolayers at both sides of the interface can be investigated separately by selective labeling with highly diluted PAC probes. At any time, the probe sites are well characterized by the electric-field-gradient tensor. The application of this method to well-defined surfaces, interfaces, and ultrathin films[17] of different materials opens a wide field of investigation.

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