VOLUME 64, NUMBER 18 PHYSICAL REVIEW LETTERS 30 APRIL 1990

Magnetic Hyperfine Field at ^{111}In Probes in the Topmost Atomic Layer of Ni(111) Surfaces

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(Received 22 January 1990)

The magnetic hyperfine field was measured at ^{111}In(^{111}Cd) probes on Ni(111) surfaces utilizing the perturbed $\gamma\gamma$-angular-correlation method. Over the entire temperature range up to the Curie temperature the magnetic hyperfine field at probes in the topmost monolayer was found to be reduced as compared to the field for probes in the 3.5th monolayer and in bulk. The probe lattice location was inferred from the structural information derived through simultaneous measurement of the electric-field-gradient tensor acting at probe nuclei.

PACS numbers: 73.20.−r, 75.30.Et, 76.80.+y

Magnetism of surfaces and thin films is the subject of continuous experimental as well as theoretical efforts. With the development of new experimental methods, interesting information has been gathered. Diffraction of spin-polarized low-energy electrons (SPLEED) allows one to determine the long-range correlation of electron spins in surface layers;[1] in electron-capture spectroscopy (ECS) scattered ions are probing the electron polarization at a distance of their closest approach, which is in the order of a few Å.[2] Formation of orthopositronium and the detection of its typical lifetime has been used to trace the electron-spin polarization near magnetic metal surfaces, where the electron density is already quite reduced.[3] Mössbauer spectroscopy has also recently been applied successfully to surfaces,[4] thin films,[5] and multilayer systems.[6] Here, the magnetic hyperfine field at probes, deposited as monolayers, serves as the quantity to study magnetic behavior at surfaces and interfaces.

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, also has a high potential for surface studies.[7] There are certain aspects which make the PAC method extremely favorable as a complementary approach to study surface magnetism. This shall be demonstrated in this Letter, where we report on the first application of this technique to magnetic surfaces.

As in Mössbauer spectroscopy, the deposition of probe nuclei permits us to study magnetism with monolayer resolution. In contrast to the Mössbauer experiments performed so far, where about one monolayer ^{57}Fe probes is needed, in PAC the concentration of probes is reduced by orders of magnitude. Because of the utilization of radioactive probe nuclei, in our case ^{111}In, even probe concentrations of about 10^{-4} monolayer (ML) are sufficient. This, on the other hand, makes it possible to study any magnetic system, since it can be labeled with PAC probes acting as isolated observers. In addition, the superior sensitivity of PAC to structural information via the electric-field gradient permits the location of probe sites.[8] This is a prerequisite in order to study the magnetic hyperfine fields at well-defined surface sites.

For the present PAC experiments we utilize the isomeric nuclear state ($I=\frac{5}{2}$, $t_{1/2}=84$ ns) intermediate between the 171-245-keV $\gamma\gamma$ cascade in ^{111}Cd, which is populated through 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 γ_1 detection. 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, which causes a time dependency of the $\gamma\gamma$-angular correlation. This time dependence is characterized by frequencies ω_n, which are transition frequencies within the nuclear sublevels. In the presence of only a magnetic hyperfine field at ^{111}In(^{111}Cd) the Larmor frequency and its first harmonic appear; in the case of a pure electric-field gradient three transition frequencies and for a combined interaction up to fifteen transition frequencies can occur.[9] With a five γ-detector setup, we record sixteen different coincidence spectra simultaneously from which eight counting-rate ratios $R(t)$ are extracted.[8] These $R(t)$ spectra can be expressed as a superposition of cosine and sine modulations containing the transition 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 the magnetic hyperfine field as well as the strength, symmetry, and 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 below 10^{-8} Pa. Disks cut from a [111]-oriented Ni single crystal were cleaned in ultrahigh-vacuum 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

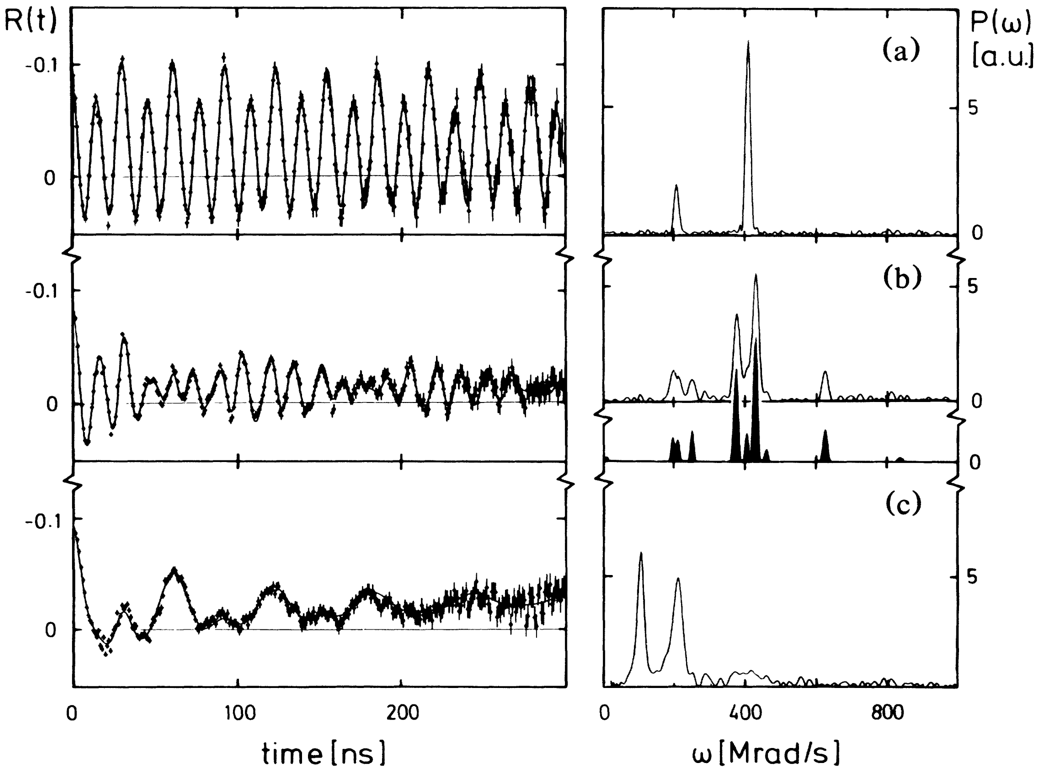

FIG. 1. PAC spectra and corresponding Fourier transforms for ^{111}In probes on Ni(111) at different measurement temperatures: (a) above the Curie temperature at $T_M = 632$ K, (b) below the Curie temperature at $T_M = 300$ K, and (c) at 100 K and after a coverage of 2.5 ML nickel. In (b) the Fourier transform of the fitted function (shaded curve) is added for comparison.

(AES). The resulting total impurity contamination was below 1% ML. Finally, radioactive ^{111}In probe atoms were deposited onto the surface with a concentration of 10^{-4} ML, which, however, introduces Cl contaminations of about 0.5% ML. The samples were then annealed to 850 K for 10 min and PAC spectra were recorded at different measurement temperatures.

Aiming at the localization of the ^{111}In probe sites on the Ni(111) surface, we first consider results for measurement temperatures above the Curie temperature $T_C = 631$ K. In this case the magnetic hyperfine field is switched off and only an electric-field gradient should be present at the probe nuclei. In fact, the frequency pattern shown in Fig. 1(a) is characteristic of the electric-field gradient at ^{111}In in substitutional terrace sites on fcc (111) surfaces, as was already established for ^{111}In on Cu(111) (Ref. 10) and Ag(111).[11] In particular, in the Fourier transform of the experimental time spectrum in Fig. 1(a), clearly two of the possible three transition frequencies are visible; the frequency ratio of 1:2 points out axial symmetry and the amplitudes together with the missing third frequency prove that the symmetry axis is normal to the surface (for details, see Ref. 8).

As an additional check, the temperature dependence of the electric-field gradient was measured above as well as below the Curie point, where, in addition, a magnetic hyperfine field is present. This is shown in Fig. 2(a), from where a strength of $|V_{zz}| = 11.4 \times 10^{17}$ V/cm^2 (at 77 K) can be read off and a weak smooth temperature dependence can be seen. All these pieces of information clearly resemble the results for Cu(111) and Ag(111) and strongly support that ^{111}In probes occupy substitutional terrace sites on Ni(111) over the whole temperature range in consideration.

Below the Curie temperature we expect the ^{111}In probes to be exposed to an electric-field gradient as well as to a magnetic hyperfine field. In Fig. 1(b) a PAC spectrum (left-hand side) recorded at 300 K is depicted. The Fourier transform of the data (right-hand side) reveals a number of transition frequencies, which can unambiguously be related to a single electromagnetic hyperfine field situation. In order to illustrate this agreement Fig. 1(b) comprises a Fourier transform of the respective fitted function in addition to the Fourier transform of the data. The extracted electric-field gradient has already been discussed above [see Fig. 2(a)]. The strength of the magnetic hyperfine field B_{hf} measured as a function of temperature is shown in Fig. 2(b). For comparison, experimental values of B_{hf} at ^{111}In on substitutional lattice sites in Ni bulk are enclosed. These

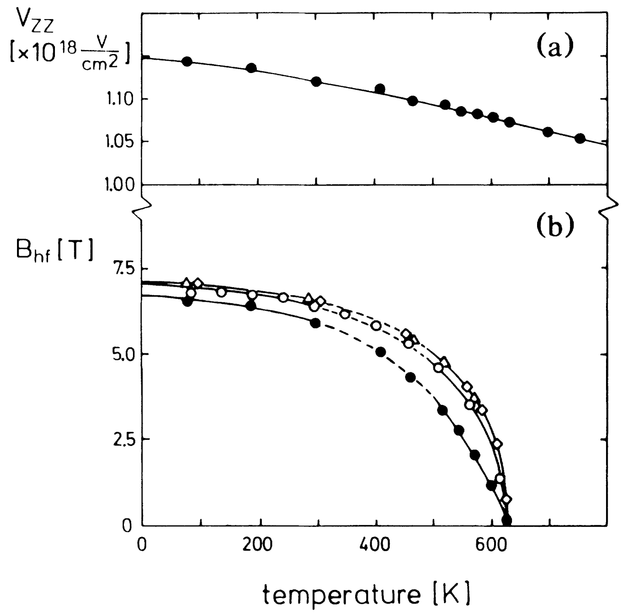

FIG. 2. Temperature dependence of the (a) electric-field gradient and (b) the magnetic hyperfine field at ^{111}In in the topmost layer of Ni(111) surfaces (solid circles), in the 3.5th monolayer (open circles), and in nickel bulk (open squares, present work; open triangles, Ref. 12). The solid lines up to 300 K are fits according to the expression $B_{hf}=B_{hf}(T=0)(1-bT^{3/2})$; the solid lines above 500 K up to the Curie point represent fits with the function $B_{hf} \propto (T_C-T)^{\beta}$.

data include results by Hohenemser *et al.*,[12] which were obtained by ^{111}In implantation into polycrystalline nickel. In addition, our own experimental data are shown, obtained from a Ni(111) surface which after the deposition of ^{111}In probes was covered by about 100 nm of nickel. Both results agree quite well within the experimental error.

The orientation of the surface magnetic hyperfine field B_{hf} is found to be temperature dependent. Above 300 K the direction of the field is lying within the (111) surface plane. Since no external magnetic field was applied, no preferred in-plane orientation of the hyperfine field can be expected. Most probably, the hyperfine field points along directions equivalent to [110], which are the second-easy axes of bulk magnetization. The easy axes in nickel bulk are along [111], which are not contained in the (111) surface plane. Below 300 K the magnetic hyperfine field tends to be tilted out of plane; at 100 K a tilt angle of 3.5(5)° is observed. This effect may be an inherent property of the surface magnetization, but a spatial relaxation of the ^{111}In impurity atoms cannot be excluded.

In order to obtain the hyperfine field near the Ni surface, we have covered an ^{111}In-labeled Ni(111) surface with an additional 2.5 ML nickel controlled by a quartz-oscillator system. The result is shown in Fig. 1(c). In this case, the electric-field gradient is expected to vanish due to the cubic symmetry of nearest- and next-nearest neighbors around the ^{111}In probes. Therefore only the magnetic hyperfine field is present, which can be recognized in the Fourier transform as the Larmor frequency $\omega_L=100(1)$ Mrad/s and $2\omega_L$. The temperature dependence of this magnetic hyperfine field is included in Fig. 2(b). Irrespective of minor deviations this dependency mainly reflects bulk behavior.

Our PAC results for the magnetic hyperfine field at a Ni(111) surface reveal remarkable features. The surface hyperfine field is smaller as compared to the bulk value over the entire temperature range up to the Curie point. In order to analyze the temperature dependency quantitatively, a $T^{3/2}$ law suggestive of spin-wave excitations was fitted to the data using the function $B_{hf}=B_{hf}(T=0)(1-bT^{3/2})$. The agreement for both surface and bulk magnetic hyperfine fields up to temperatures of about 300 K is reasonable; however, an exponent of 2.5 would improve the quality of the fits.

For the parameter b, a value of $b_{surf}=2.4(2)\times 10^{-5}$ K$^{-3/2}$ is obtained for the surface hyperfine field, which is about 50% higher than the value $b_{bulk}=1.6(2)\times 10^{-5}$ K$^{-3/2}$ derived for ^{111}In in the 3.5th ML and in bulk. A similar effect was detected by Korecki and Gradmann in comparing the magnetic hyperfine field at ^{57}Fe for Ag-covered Fe(110) surfaces with Fe thin films,[13] which is discussed in terms of a loss of exchange bonds across the surface leading to standing spin waves.[14] On the other hand, for Ni(111) Rau and Kuffner[15] detected a rather linear dependence of the electron polarization in the range from 300 K up to the Curie temperature as determined by electron-capture spectroscopy. Mean-field calculations by Kisker[16] for the magnetization of the Ni(111) surface monolayer agree fairly well with the electron-capture-spectroscopy data. However, they do significantly deviate in the case of the bulk magnetization, which in its turn scales as B_{hf} found for ^{111}In in Ni bulk.

The surface magnetic hyperfine field, extrapolated to $T=0$ K employing the $T^{3/2}$ dependence, turns out to be reduced by about 7% [$B_{hf}(T=0)=6.7(1)$ T] as compared to the bulk value [$B_{hf}(T=0)=7.2(1)$ T]. This effect, actually a reduction of 15%, is predicted by Freeman *et al.*[17] for B_{hf} at nickel probes on Ni(100) surfaces. This is qualitatively understood in terms of a considerable change of the conduction-electron density at the surface, which leads to a diminished Fermi contact field at the probe nuclei. Experimentally, this was also noticed for Fe probes on Fe(110), where a reduction of about 5% was identified.[13]

Finally, it is instructive to inspect the behavior of B_{hf} close to the Curie point. Within experimental errors no indication for a shift of the Curie temperature for ^{111}In in the topmost layer is given. Analysis of the B_{hf} behavior in the temperature interval from 500 K up to the Curie point exhibits an experimental dependence well described by the commonly used function $B_{\rm hf} \propto (T_C - T)^\beta$, with β being the critical exponent for temperatures close to the Curie temperature [T_C(Ni) = 631 K]. For ^{111}In probes in the surface we find $\beta_{\rm surf} = 0.70(9)$; for bulk $\beta_{\rm bulk} = 0.37(5)$ is extracted, which agrees with $\beta_{3.5\,\rm ML} = 0.40(5)$ obtained for ^{111}In in the 3.5th monolayer. Although no β exponent for Ni(111) surfaces has yet been published, a comparison with previously obtained β values for Ni(100) and Ni(110) surfaces is quite informative. For Ni(100) surfaces, SPLEED experiments[18] reveal $\beta_{\rm surf} = 0.79(2)$; in the case of Ni(110), the critical exponent is found to be $\beta_{\rm surf} = 0.77(2)$ utilizing SPLEED (Ref. 19) and $\beta_{\rm surf} = 0.70(10)$ measuring positronium decay.[3] On the other hand, for Ni bulk a value of $\beta_{\rm bulk} = 0.358(3)$ was determined earlier.[20,21] Our results are in excellent agreement with all the results quoted above.

In conclusion, we have demonstrated that with the PAC method the magnetic hyperfine field can be measured with high accuracy over the entire interesting temperature range. The location of our PAC probes is well determined through the measured properties of the electric-field-gradient tensor. The magnetic hyperfine field can be distinguished for probes dwelling at the surface as well as in near-surface layers and finally in bulk. This permits the study of the hyperfine parameters as a function of depth with monolayer resolution. The labeling of the system with only about 10^{-4}-ML PAC atoms opens up prospects to apply PAC to many other magnetic surfaces as well as to ultrathin magnetic layers and interfaces.

The authors thank T. Klas and R. Wesche for continuous help and interest and W. Schulter and his colleagues in the workshop for the excellent technical assistance. The generous financial support by the Deutsche Forschungsgemeinschaft, Bonn (Sonderforschungsbereich No. 306) is gratefully acknowledged.

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