Electron-Spin Polarization at Single-Crystalline Cr and Ni Surfaces Determined with Electron-Capture Spectroscopy

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The spin polarization P of electrons at Cr and Ni surfaces is measured with electron-capture spectroscopy. With use of one-electron capture at magnetized Cr(100)-$c(2\times 2)$ surfaces at 293 K ($T_N = 310$ K), P values up to -18% are found revealing ferromagnetic order at this surface. Utilizing two-electron capture at demagnetized Ni surfaces we find at 293 K ($T_C = 631$ K) $|P| = 94\%$ for Ni(110), $|P| = 72\%$ for Ni(100), $|P| = 47\%$ for Ni(111), and $|P| = 14\%$ for Ni(120). There is evidence that "local" ferromagnetic order at Ni surfaces exists even at $2T_C$.

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For some years past there has been an increasing scientific interest and activity in studies on surface magnetism.[1,2] Particularly surfaces of transition metals such as Ni, Fe, and Cr are investigated because of their technological importance as commercial catalysts. Rapid theoretical progress in developing reliable and accurate methods for surface electronic structure calculations,[3] including magnetic phenomena where self-consistency is important and the development of powerful experimental tools (photoemission and field emission,[4] electron capture,[5] tunneling,[6] scattering of spin-polarized electrons,[7] UHV magnetometer[8]) for the investigation of the magnetic structure of surfaces, now opens a most promising way to answer fundamental questions in surface magnetism. Does ferromagnetic order exist at the surface of a bulk ferromagnetic or antiferromagnetic material? What changes at the Curie or Néel temperature? Theoretical and experimental data on the electron-spin polarization (ESP) at the surfaces of these materials give a direct answer to these challenging questions.

In this Letter we report on ESP measurements using electron-capture spectroscopy (ECS)[5,9,10] at atomically clean and flat surfaces of Cr and Ni single crystals. The basic process in ECS is the capture of one or two spin-polarized electrons during grazing-angle surface reflection of fast (150-keV) deuterons. The distance of closest approach of the ions during the specular reflection (incidence angle 0.2°) amounts to about 0.2 nm, showing that the ions probe in real space only the exponential tail of the electronic wave functions at the surface.[5,9,10] This reveals the extreme surface sensitivity of ECS. Figure 1 gives a schematic representation of the experimental setup.

Detection of ESP involving one-electron capture (OEC).—A well collimated beam (half angle of divergence $<0.025°$) of 150-keV deuterons is reflected and thereby partially neutralized at a (hkl) surface of a ferromagnetic (or antiferromagnetic) single crystal magnetized to saturation parallel to the surface plane. After reflection the beam passes through an electric field to extract positive and negative charged ions. Therefore only neutralized particles impinge on a T target and provide α particles via the reaction $\mathrm{T}(d,n)\alpha$. During an adiabatic transition from the high magnetic field region at the magnetic surface into a weak magnetic guiding field, part of the ESP in the electron shell of the neutralized atoms is converted into a nuclear polarization by hyperfine interaction. The nuclear polarization which serves as a measure of the ESP is determined via the T reaction using the α-counting ratio $r = N_z/N_y$ in two α solid-state detectors (12, 13 in Fig. 1). Defining P along the $+z$ direction (see Fig. 1) we obtain

$$P = (n^+ - n^-)/(n^+ + n^-), \tag{1}$$

where n^+ and n^- represent fractional numbers of

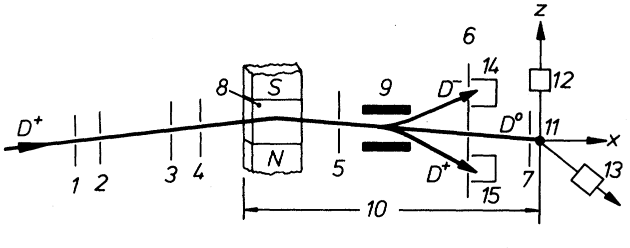

FIG. 1. Experimental arrangement: (1)–(7), ion-beam collimating slits; (8) ferromagnetic target (12 × 8 × 1.5 mm^3), magnetized perpendicular to the incoming beam direction; (9) electrostatic condensor; (10) weak magnetic field (0.8 mT), parallel to the target magnetizing field used as quantization axis (+z direction) in OEC experiments; (11) T Ti target; (12) and (13), α solid-state detectors; (14) and (15), Faraday cups.

electrons with spin moment antiparallel and parallel, respectively, to the target magnetizing field. The ESP is directly related to r[5,9]:

$$P = 12(1-r)/(r+2). \qquad (2)$$

The target magnetizing field is applied to align randomly oriented Weiss domains, thereby producing a macroscopic magnetization which defines a preferred direction in space along which the sign and magnitude of P can be measured.

Detection of ESP involving two-electron capture (TEC).—A beam of 100-keV deuterons is reflected at a demagnetized surface of a ferromagnetic single crystal. After reflection the beam passes through an electric field to split spatially the D^- and the D^+ ions. The D^- and the D^+ ion currents are then simultaneously detected with use of two Faraday cups (14, 15 in Fig. 1). Contrary to OEC, which can be used to detect long-range ferromagnetic order at surfaces, TEC probes "local" ferromagnetic order at surfaces on a microscopic scale. Since the lateral interaction length of a deuteron with the reflecting surface is only a few hundred atomic diameters which is much smaller than the lateral dimensions (micrometers–millimeters) of ferromagnetic domains, it is obvious that two electrons captured by a single deuteron always possess the same spin alignment given by the direction of the spontaneous ferromagnetic order existing in each domain also in demagnetized samples below T_C. Two electrons in a domain have either parallel or antiparallel spin directions corresponding to a triplet or singlet final state in a formed D^- ion. Using deuterons (or protons) for TEC we note that for D^- ions only singlet-$(1s^2)$ states exist. Triplet states such as $D^-(1s2s)$ with two electrons with spin aligned parallel do not exist.[11-13] Consequently, the formation of D^- ions should be drastically suppressed for ferromagnetic surfaces with an ESP of + 100% or − 100%. For surfaces of nonmagnetic materials such as Cu where the electrons are nonpolarized the formation of D^- ions will not be suppressed. At present no theoretical treatment of D^- formation and survival during surface reflection of high-energy deuterons is available.[14] Therefore, in a simple first approximation we relate the measured charge-state ratio $R = D^-/D^+$ (D^- fraction of the reflected beam; D^+ fraction of the reflected beam) at Ni and Cu surfaces directly to the corresponding fractional numbers n_{Ni} and n_{Cu} for Ni and Cu surface electrons, respectively:

$$R_{\mathrm{Ni}}/R_{\mathrm{Cu}} = n_{\mathrm{Ni}}/n_{\mathrm{Cu}}. \qquad (3)$$

With $P=0$ for Cu and $n_{\mathrm{Cu}}^+ + n_{\mathrm{Cu}}^- = 1$ we get from Eq. (1) $n_{\mathrm{Cu}}^+ = n_{\mathrm{Cu}}^- = n_{\mathrm{Cu}} = 0.5$. For Ni the negative-ion formation rate determining fractional electron number is $n_{\mathrm{Ni}} = (1-|P|)/2$ with $n_{\mathrm{Ni}}^+ + n_{\mathrm{Ni}}^- = 1$. We then obtain for P

$$|P_{\mathrm{Ni}}| = 1 - (R_{\mathrm{Ni}}/R_{\mathrm{Cu}}). \qquad (4)$$

Note that spin-flip processes between the negative ions and the solid are negligible because the particles interact only for a time of 10^{-14} s in the close vicinity of the surfaces whereas spin-flip processes occur in a time scale of 10^{-12} s.[15]

Chromium.—The 3*d* metal Cr is antiferromagnetic below the Néel temperature $T_N = 310$ K and consists of two compensating ferromagnetic sublattices. In the (100) direction the spin structure is sinusoidal and incommensurate with the lattice period. Therefore one might expect ferromagnetic order at the topmost surface layer of Cr(100).

The Cr(100) crystal is prepared with a surface orientation better than 0.01°. After several standard cleaning-annealing procedures the final C and O contaminations are less than 0.02 monolayer as monitored with Auger electron spectroscopy. Low-energy electron-diffraction measurements show a $c(2\times 2)$ surface structure. The ESP is investigated at 2×10^{-11} mbar with ECS involving OEC. Increasing the applied magnetizing field B up to 0.09 T we find at 293 K an ESP up to − (18 ± 2)% clearly showing the existence of long-range ferromagnetic order at this surface below T_N. At 365 K zero ESP is detected. These findings can serve as a crucial test for the ability of mathematical approaches to describe the surface electronic structure of antiferromagnetic materials. At present only one calculation[16] is available where within a simple tight-binding approximation it is shown that the Cr(100) surface is ferromagnetic. Note that no evidence is found for surface reconstruction of Cr(100).

Nickel.—The Ni and Cu crystals undergo the same treatments as described for Cr. For ECS involving TEC we apply 100-keV deuterons at 0.2° grazing incidence on diverse Ni(*hkl*) and Cu(*hkl*) surfaces. We remark that during the 0.2°-grazing-angle reflection of the ions 0.2 nm outside the surface, electrons in the highest occupied states are overwhelmingly those available for capture.[5] In *k* space these are electrons near the Fermi level. The results of these systematic studies performed at 413 K are listed in Table I together with the corresponding $|P_{\mathrm{Ni}}(hkl)|$ data. In addition we have listed in Table I data on the ESP at Ni(*hkl*) surfaces measured with spin-po-

TABLE I. Experimental data on the ESP at Ni surfaces.

			ECS		
		TEC		OEC	PES
(hkl)	$10^3 R_{\mathrm{Ni}}$	$10^3 R_{\mathrm{Cu}}$	$\lvert P\rvert$ (%)	P (%)	P (%)
(110)	0.35	5.70	94	−96	-95^{a}
(100)	1.45	5.25	72	−64	-30^{b}
(111)	3.05	5.75	47	−45	-45^{c}
(120)	4.62	···	14^{d}	+15	···
polycr.	···	5.37^{d}			

[a] Ref. 17.
[b] Ref. 18.
[c] Ref. 19.
[d] Ref. 20.

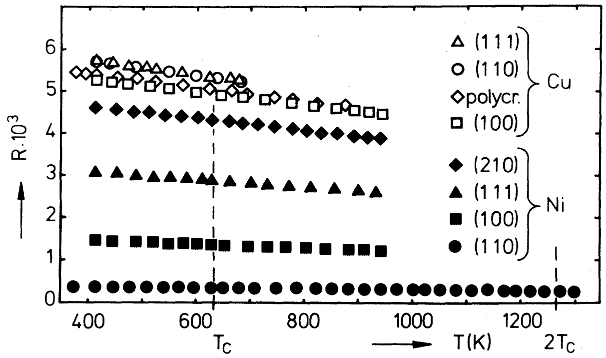

FIG. 2. Charge-state ratios $R_{\mathrm{Ni}}\,(hkl)$ and $R_{\mathrm{Cu}}(hkl)$ as functions of the target temperature T. Polycr. refers to polycrystalline Cu. For Ni only each second measuring point is drawn in order to give a clear plot.

larized photoemission spectroscopy (PES) and with ECS using OEC.[5] From the comparison of the respective ESP values one is tempted to assume that already the rigorous evaluation of $|P|$ as given by Eq. (4) is useful to determine surface magnetic order although at present a proper theoretical treatment of TEC for grazing-angle reflection is not available.

In Fig. 2 measurements on the temperature dependence of R at various Ni and Cu surfaces are shown. Numerous experimental difficulties had to be overcome to maintain clean surfaces during the multiple heating and cooling cycles necessary if reliable data on the R values are to be obtained.[21] At all temperatures C, S, and O coverages are less than 0.02 monolayer. The temperature of the samples is kept constant within 0.03°, the absolute temperature being calibrated within 0.5°.

As seen from Fig. 2, the $R_{\mathrm{Cu}}(hkl)$ data exhibit with respect to the different surface orientations only a small splitting. This can be caused by an (hkl)-dependent variation in the surface work function $\varphi_{\mathrm{Cu}}(hkl)$ which at maximum amounts to $\Delta\varphi = 0.50$ eV.[22] For Ni $\Delta\varphi$ is even smaller (0.31 eV),[22] implying that the rigorous evaluation of $|P|$ from Eq. (4) is reasonable. We note, however, that the uniform decrease of the $R_{\mathrm{Ni}}(hkl)$ and $R_{\mathrm{Cu}}(hkl)$ data with increasing temperature can be correlated with the decrease of the corresponding $\varphi_{\mathrm{Ni}}(hkl)$ and $\varphi_{\mathrm{Cu}}(hkl)$ values with increasing temperature which is known to be independent of surface orientation.[23]

From Fig. 2 we see that there is no drastic increase of the $R_{\mathrm{Ni}}(hkl)$ data near T_{C} as one would expect in a conventional picture of ferromagnetism where, as a result of the disappearance of exchange-induced energy band shifts beyond T_{C}, equal numbers of up- and down-spin electrons are available. Our present results suggest that "local" ferromagnetic order exists on an atomic scale for Ni far above T_{C}, e.g., for Ni(110) up to $2.05T_{\mathrm{C}}$, implying that the ferromagnetic exchange splitting is temperature independent as stated in modern theories where the finite-temperature properties of the $3d$ transition metals are treated in the frame of a "local band" picture where the interatomic exchange gives rise to ferromagnetism.[24-27] We remark that Slater[28] already in 1968 pointed out that there is no interrelation between the ferromagnetic exchange splitting and T_{C} which is characterized only by the disappearance of long-range spin order, whereas the energy separation between up- and down-spin electron bands is correlated with exchange effects occurring on an atomic scale.[29] In conclusion we state that our experimental findings pose a framework for future spin-polarized surface electronic structure calculations on the finite-temperature properties of $3d$ transition metals.

Work is in progress to study TEC processes with use of other ions than deuterons, e.g., He^{++} ions, where the relative intensities in light emission from excited singlet and triplet atomic states can also be used to detect surface magnetic order.

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[20] For the evaluation of $|P_{\mathrm{Ni}}(120)|$ we have used R_{Cu} (polycrystalline) because no Cu(120) crystal was available.

[21] Note that in ECS experiments there is a beam-cleaning effect that helps to maintain a clean surface.

[22] For Cu the work functions are $\varphi(110) = 4.48$ eV, $\varphi(100) = 4.59$ eV, $\varphi(111) = 4.98$ eV giving $\Delta\varphi = 0.50$ eV [cf. P. O. Gartland, Phys. Norv. 6, 201 (1972)]. For Ni the corresponding data are $\varphi(110) = 5.04$ eV, $\varphi(100) = 5.22$ eV, $\varphi(111) = 5.35$ eV giving $\Delta\varphi = 0.31$ eV [cf. B. G. Baker, B. B. Johnson, and G. L. C. Maire, Surf. Sci. 24, 572 (1971)].

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Nuclear-Spin Relaxation in Two-Dimensional Metals at High Magnetic Fields: $Hg_{3-\delta}AsF_6$

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An unusual linear dependence of the nuclear-spin relaxation rate upon the magnetic field is observed in the incommensurate linear-chain mercury compound $Hg_{3-\delta}AsF_6$. It is shown that in two-dimensional metals the planar cyclotron motion of the conduction electrons in a strong magnetic field gives rise to a divergence of the spin-spin correlation function. This new effect, combined with the small orbits resulting from the incommensurate structure, can explain the observed nuclear-spin relaxation behavior in the pseudo two-dimensional metal $Hg_{3-\delta}AsF_6$.

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The mercury nuclear spin-lattice relaxation rate in the linear-chain mercury compound $Hg_{3-\delta}AsF_6$ was observed to display an unusual, strong dependence on magnetic field at liquid-helium temperatures; namely, the rate *increased* considerably with the magnetic field.[1] Electrical transport studies show this compound to behave as a relatively clean metal at low temperatures with strong temperature dependence of the resistance and no indication of residual resistivity.[2,3] Nuclear relaxation in such clean metals is usually field independent and obeys the Korringa law. The linear-chain structure[4,5] of $Hg_{3-\delta}AsF_6$ restricts the motion of the conduction electrons