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STRONG TEMPERATURE DEPENDENCE OF FERROMAGNETISM AT Ni and Tb SURFACES DETERMINED WITH ELECTRON CAPTURE SPECTROSCOPY ECS*

C. RAU, E. UMLAUF[+] and H. KUFFNER‡

Physics Department, Rice University, Houston, TX 77251, USA

The magnetic structure of the topmost atomic layer of Ni and Tb surface has been investigated using electron capture spectroscopy (ECS). Contrary to bulk behavior, at Ni(111) surfaces, the long-range magnetic order, characterized by the long-range electron spin polarization (ESP), decreases from −43% at $T = 293$ K almost *linearly* to zero at the bulk Curie temperature $T_{Cb} = 631$ K. The "local" surface magnetic order (SMO) at Ni(111) surfaces is temperature independent and is detected far above T_{Cb}. At Tb surfaces, however, the "local" SMO is strongly temperature dependent and disappears above T_{Cb}.

1. Introduction

At present there is an increasing scientific and technological interest in a deeper comprehension of ferromagnetism in connection with surfaces. Rapid theoretical and experimental advances in this field now open a promising way to answer many fundamental questions about surface magnetism [1,2]: Is the temperature dependence of the surface magnetic order (SMO) different from bulk magnetic behavior? What changes at the critical temperatures? Considerable theoretical work is centered upon the influence of a surface on magnetic phase transitions [3]. Thus, there is large interest in any available experimental results on the temperature dependence of the SMO which is well characterized by the electron spin polarization (ESP) [2,4]. ESP-data recorded over a wide range of temperatures T above and below the critical temperature are therefore highly desirable, as are ESP-data measured very close to the critical temperature.

The primary reason for the lack of sufficient experimental data is strongly related to difficulties in the preparation of atomically clean surfaces which remain uncontaminated and well-defined during multiple heating and cooling cycles which are necessary to obtain reliable data. The other reason is, that there are only a few experimental techniques which allow one to record data over a wide range of temperatures. Intrinsic surface effects can only be detected if the experimental probing depth of the applied technique is of the order of the spin–spin-correlation length which amounts to about a lattice constant for temperatures not too close to the critical temperature. At the critical temperature the spin–spin-correlation length diverges causing surface effects to extend deep into the bulk.

In this paper we report on the temperature dependence of the long-range and "local" surface magnetic order for Ni which is the prototype of an itinerant 3d-electron band ferromagnet, and for Tb which is the prototype of a localized 4f-electron Heisenberg ferromagnet. The SMO is investigated with electron capture spectroscopy (ECS) [2,5] at the *topmost* atomic layer of atomically clean and flat Ni(111) surfaces between 293 K and 940 K. It is found that – contrary to the well-known bulk magnetization of Ni – the long-range ESP decreases almost *linearly* from −43% at 293 K until it drops to zero at the bulk Curie temperature T_{Cb} and remains zero above T_{Cb}. The "local" SMO is found to be nearly temperature independent existing still at temperatures far above T_{Cb}. Such behavior is only found for Ni. At Tb surfaces, however, the "local" SMO is found to be strongly temperature dependent disappearing above T_{Cb}.

2. Experimental

In ECS, unpolarized deuterons impinge at grazing incidence on clean and flat surfaces of magnetic materials. The fundamental process in this kind of spin spectroscopy is the capture of one or two spin-polarized electrons during the small angle reflection of the deuterons [2,5,6]. For an angle of incidence of 0.2°, the distance of closest approach of the ions to a surface amounts to about 1–2 Å. Thus, the deuterons probe the spin-polarized local electron densities of state at the *topmost* surface layer.

Fig. 1 gives a basic representation of the experimental configuration used to measure the long-range and the "local" magnetic order at surfaces of magnetic materials. A well collimated (half-angle of

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[+] Walter-Meissner-Institute f. Low-Temp.-Res., Bav. Acad. Sci., D8046 Garching, F.R.G.

‡ Present address: Siemens AG. Munich, F.R.G.

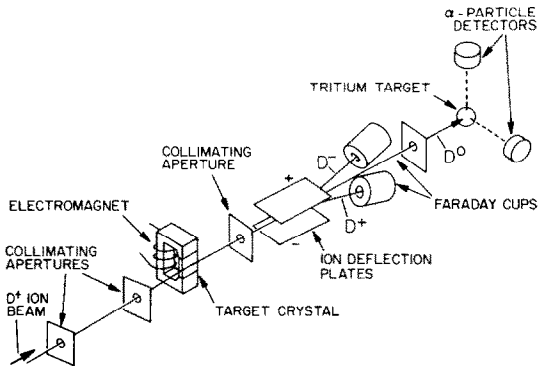

Fig. 1. Schematic diagram of the apparatus used in ECS experiments.

divergence $< 0.025°$) beam of 150 keV deuterons is reflected at grazing angle on the target, which is magnetized parallel to the surface plane, and perpendicular to the incoming beam direction. Specularly reflected particles then enter a transverse electric field which spatially separates the remaining D^+ from D^0 and D^- ions formed by one- and two-electron capture, respectively. The D^+ and D^- ion currents are recorded in two Faraday cups providing a measure of the "local" ESP [6]. The D^0 atoms impinge on a tritium target where their nuclear polarization is determined via the asymmetry in the angular distribution of the α-particles emitted in the reaction T(d, n)α. A weak magnetic field, parallel to the target magnetizing field, provides a well-defined quantization axis.

For the measurement of long-range surface magnetic order we employ one-electron capture processes [2,5]. A target magnetizing field is applied to align randomly oriented Weiss domains thereby producing a macroscopic magnetization along which the sign and magnitude of the ESP can be measured. At ferromagnetic surfaces, one-electron capture processes result in the formation of deuterium atoms possessing a net electron spin polarization. This ESP is partially converted by hyperfine interaction to a deuterium nuclear polarization which provides a measure of the net ESP of the captured electrons.

Defining the ESP, P, along the target magnetizing field yields $P = (n^+ - n^-)/(n^+ + n^-)$, where n^+ and n^- represent fractional numbers of electrons with spin moment antiparallel (majority spin electron) and parallel (minority spin electron), respectively, to the target magnetizing field. Because the electrons captured by different deuterons originate at widely separated points on the sample surface, long-range ESP is detected with one-electron capture measurements.

In addition to the measurement of the long-range surface magnetic order, ECS allows us to investigate "local" SMO employing two electron capture processes. Here the situation is significantly different. The only stable bound state of D^- is the $1s^2\,{}^1S$ state. D^- can therefore only be formed by capture of electrons with opposite spins. From the present understanding of the physics of two-electron capture processes, the characteristic length within which these processes occur is small, ~10–20 Å for 150 keV deuterons. Thus, the captured electrons must originate in the same "local" surface region, and two-electron processes will be strongly suppressed by the presence of "local" surface magnetic order. The reduction in the D^-/D^+ ratio in the reflected beam, relative to that for a nonmagnetic target such as Cu, therefore, provides a direct measure of the "local" ESP existing at a surface on an atomic scale within a few atomic neighbors [2,6].

Numerous experimental difficulties were overcome in order to maintain clean surfaces during multiple heating and cooling cycles. In the case of Ni(111), at all temperatures C, S, and O coverages were shown to be less than 0.02 monolayer using a cylindrical mirror analyser for Auger analysis at each measuring point. In the case of polycrystalline Tb, however, the residual C and O contaminations could not be reduced in these measurements below 0.05 monolayer for C and 0.15 monolayer for O. This will be further discussed in section 3.

3. Results and discussion

The upper part of fig. 2 gives experimental results on the long-range ESP (see ● in fig. 2) measured with ECS at atomically clean and flat single-crystalline surfaces of Ni(111) as a function of the reduced temperature $t = T/T_{Cb}$. At 293 K ($t = 0.5$) the ESP amounts to −43% and decreases almost *linearly* with increasing T until it drops to zero at T_{Cb}. This behavior of the long-range ESP is drastically different from the magnetization of bulk Ni. The lower part of fig. 2 shows a plot of the magnetization of layers parallel to the (111) surface of a fcc ferromagnet like Ni in the mean-field model (taken from ref. [8]; see also refs. [7,9]). The long-range ESP measured with ECS at the topmost surface layer closely follows the T behavior of the magnetization for the topmost surface layer, as predicted by the mean-field model, which is expected to be qualitatively correct (In electron capture spectroscopy using two-electron capture demagnetized samples can be measured [6].) when the spin–spin correlation length is not large compared to the lattice spacing ($t < 0.9$).

The T-dependence of the "local" surface magnetic order (see ▲ in fig. 2) reveals significantly different behavior. The magnitude of the "local" ESP [6,10] amounts to about 47% and remains constant until the highest measured temperature of 940 K ($t = 1.5$), which is far above T_{Cb}. This behavior implies that electron

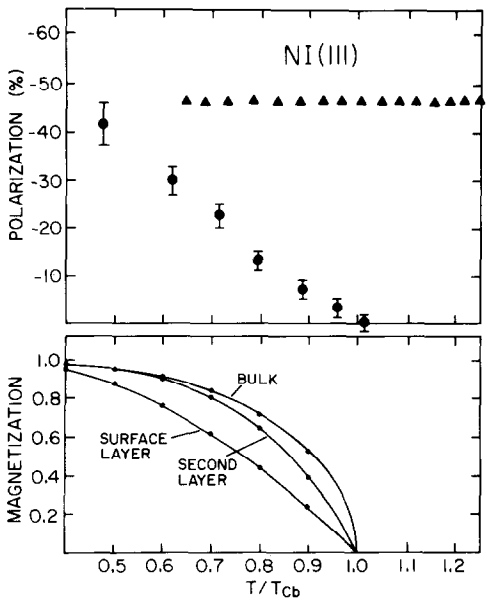

Fig. 2. Upper part: T-dependence of the long-range ESP (●) and of the "local" ESP (▲) at Ni(111) surfaces. Lower part: T-dependence of the first and second layer and the bulk in mean field theory [8].

exchange effects between minority and majority spin electrons from nearby atoms are temperature independent. This behavior of the "local" ESP is only found for the itinerant electron 3d-transition metal Ni.

For localized 4f-electron Heisenberg ferromagnets such as Tb, one expects different behavior. Above the Curie temperature, where the transition from ferro- to paramagnetic behavior occurs, one expects that the alignment of the 4f spins disappears on an atomic scale. This should also be revealed in a disappearance of the "local" surface magnetic order of the conduction electrons. In the first experiments we selected the 4f rare-earth metal Tb, which is ferromagnetic below $T_{Cb} = 220$ K, antiferromagnetic with a helical spin structure up to its Néel temperature $T_{Nb} = 228$ K, and paramagnetic above this temperature [13]. At 200 K we find a "local" ESP of 68% which decreases to 56% at 250 K and to 15% at 270 K and disappears around 300 K. Decreasing the temperature again to 200 K, the previously measured ESP data can be restored. We remark that the "local" ESP values measured so far have to be considered as lowest limits. Tb-oxides, which are possibly present as TbO_2 or Tb_2O_3 possess Néel temperatures below 14 K [12], and therefore can only lower the intrinsic "local" ESP at the atomically clean Tb surface. More refined ECS measurements at Tb surfaces are underway to determine the intrinsic "local" surface magnetic order and also the long-range ESP at atomically clean Tb surfaces where the C and O contamination is kept below 0.02 monolayer.

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