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Temperature-dependent surface magnetization of FeNi₃(111) studied by spin-resolved appearance potential spectroscopy

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Abstract. The temperature-dependent magnetic properties of the FeNi₃(111) surface were investigated by means of spin-resolved appearance potential spectroscopy. Within the temperature range studied, from 100 K to 1100 K, two phase transitions occur in the bulk: a compositional order–disorder phase transition between 770 and 785 K and a ferromagnetic–paramagnetic phase transition with a Curie temperature of 863 K. The first one does not show up in the appearance potential signals of Fe and Ni, while the latter is reflected in the spin-asymmetry signals. Both the Fe and the Ni signals follow the bulk magnetization curve of FeNi₃ with no evidence of any exceptional surface magnetic properties. Furthermore, our data show that, to a good approximation, the spin asymmetry of the appearance potential signal is proportional to the magnetization.

1. Introduction

The phase diagram of Fe_xNi_{1-x} alloys contains a variety of structural, mechanical, and magnetic properties, which provided the impetus for numerous research studies and led to diverse applications [1]. In particular, alloys with about 80% Ni, all with face-centred-cubic (fcc) crystal structure, exhibit almost zero magnetostriction and a very high permeability; they are therefore called permalloys. At and near the composition FeNi₃, the alloys can undergo long-range ordering in the Cu₃Au structure below a temperature of 770 K, but with a strongly reduced permeability. The compositional (dis)order of FeNi₃ was extensively studied both experimentally [2–7] and theoretically [8–11]. The experimental studies probed bulk properties by means of, e.g., x-ray diffraction, neutron diffraction, and Mössbauer spectroscopy.

X-ray photoelectron spectroscopy (XPS) was used to investigate the electronic structure of FeNi₃ in the ordered and disordered state [12]. The 2p levels of Fe and Ni were observed to be unchanged, except that the Fe line showed some broadening in the disordered state. However, the state of order of the surface region, to which XPS is sensitive, was not characterized. Surface-sensitive studies by means of Auger-electron spectroscopy (AES) indicate an enrichment of Ni at or near the surface [13]. Oxidation of the samples, on the other hand, leads to an enrichment of Fe in the surface region [14].

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To our knowledge, the first surface-sensitive study on a single crystal of FeNi₃ was performed by means of spin-polarized low-energy electron diffraction [15]. The (111) surface of FeNi₃ was found to exhibit an enhanced Curie temperature compared with the bulk, combined with an antiparallel magnetic coupling between the surface and the bulk.

In this paper we aim to study the FeNi₃(111) surface using a surface-sensitive and element-specific technique which provides magnetic information: spin-resolved appearance potential spectroscopy (APS) [16–19]. Electrons of variable energy are used to excite core electrons into empty states above the Fermi level E_F . The measured signal monitors the recombination of the core holes created, via Auger-electron emission or soft-x-ray emission [20]. The latter is realized in our experiment; the technique is therefore called soft-x-ray APS. During an energy sweep of the incoming electrons, an increase in the total emission yield is detected as soon as a further core level is available for excitation. Since both the exciting and the excited electrons are scattered into empty states, the rate of possible excitations and, thereby, also that of detected recombinations depend on the density of states above E_F . APS is a core-level spectroscopy which probes the local electronic structure with a probing depth of about six atomic layers in the energy range under investigation. Using spin-polarized electrons gives access to the spin-dependent local electronic structure above E_F . This technique should be able to monitor the magnetic properties of the surface for Fe and Ni separately and to help to explain the origin of the exceptional magnetic properties, if present.

2. Experiment

Our experiments were performed in an ultra-high-vacuum chamber with a base pressure of 3×10^{-9} Pa. The pressure did not exceed 1×10^{-8} Pa during the measurements over the entire range of sample temperatures from 100 K to 1100 K.

The sample was an FeNi₃ single crystal with a (111) surface, clamped onto a horseshoe magnet to provide magnetization in the surface plane along the $\langle 110 \rangle$ directions. *Extra situm* microscopy using the magneto-optic Kerr effect (MOKE) showed a complex domain structure in remanence. Magnetization in a single-domain state was only achieved by applying an external field. The field was produced by a magnetization coil wound around the horseshoe magnet. Due to the closed-circuit geometry for the magnetic flux, the magnetic stray fields were kept to a minimum. No influence on the electron spin polarization was detected. All of the APS measurements were obtained with the sample in a saturated single-domain magnetic state; this was achieved by applying an external field. Magnetic saturation was proved by *in situ* MOKE hysteresis curves.

For preparing the ordered state of the sample, the crystal was heated to 743 K for more than 100 h before preparing the surface. According to reference [4] this should result in an ordered state where the disordered phase disappears and the ordered domains with an average size of about 80 Å come into contact. As a consequence, APS measurements on FeNi₃ prepared in that way are expected to represent the ordered state. Then the (111) surface was cleaned by cycles of sputtering with 900 eV neon ions and subsequent annealing to 700 K. This cleaning procedure was repeated until no contaminants were detected with a four-grid retarding-field Auger-electron spectrometer. The main contamination of the surface was sulphur which diffuses from the bulk onto the surface at elevated temperatures. The sample temperature was adjusted either by cooling with liquid N₂ or heating via electron bombardment. To measure the disorder at low temperatures, the sample was cooled at up to 3 K s^{-1} from above the order–disorder transition temperature. According to the literature [2], this should result in a low-temperature disordered phase in the bulk. It should be noted,

however, that we had no means of determining the degree of order in the bulk. We followed the preparation recipes published in the literature as described above [4]. Whether or not the surface adopts the state of order of the bulk with the same or a different transition temperature is not clear to this day. The high-temperature data had to be measured during electron bombardment onto the rear side of the sample. Careful shielding of the sample was necessary to prevent x-rays, caused by the heating process, from burying the soft-x-ray APS signal.

The apparatus for spin-resolved appearance potential spectroscopy (APS) consisting of a spin-polarized electron source and a soft-x-ray detector is described in detail elsewhere [21, 22]. Briefly, a spin-polarized electron beam of typically 30 to 60 μA is emitted from a GaAs photocathode irradiated with circularly polarized laser light. The data presented are renormalized to a hypothetical electron spin polarization of 100% which eliminates the influence of the incomplete experimental beam polarization ($\approx 30\%$). The APS signal is detected via soft-x-ray emission. It is measured by modulating the electron energy and monitoring the first derivative by means of a lock-in technique. Details of the APS measurement can be found in publications on the low-temperature data for Fe and Ni [17] as well as FeNi_3 [19].

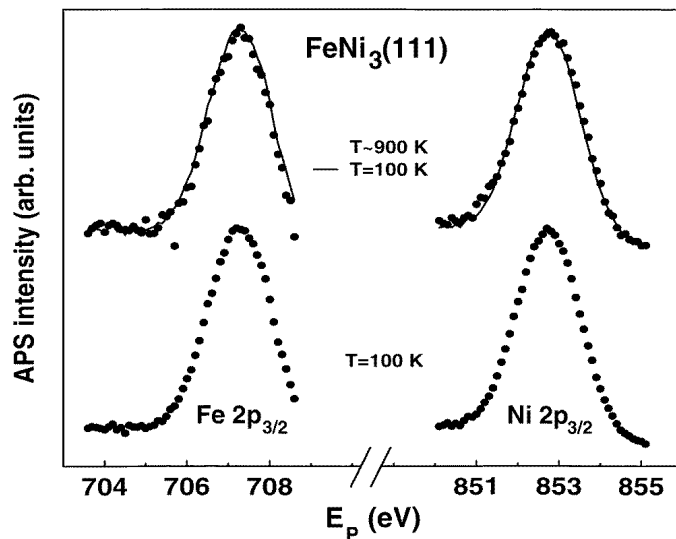


Figure 1. Spin-integrated data for the APS main line for $\text{Fe } 2p_{3/2}$ and $\text{Ni } 2p_{3/2}$ in $\text{FeNi}_3(111)$ at $T = 100 \text{ K}$ and at $T \approx 900 \text{ K}$, i.e. above the Curie temperature. For the purposes of comparison, the low-temperature data are included in the high-temperature data as a solid line.

3. Results

First of all, we looked for any change of the APS line shape as a function of temperature in a spin-integrated measurement. As the potential modulation, a peak-to-peak voltage V_{p-p} of 2 V was chosen. This value ensured high APS signals for the $2p_{3/2}$ levels of Fe and Ni without modulation-induced broadening effects. Figure 1 shows spin-integrated measurements of the main APS lines for $\text{Fe } 2p_{3/2}$ and $\text{Ni } 2p_{3/2}$ at $T = 100 \text{ K}$ and $T \approx 900 \text{ K}$. The first derivative of the soft-x-ray yield is shown as a function of the primary-electron

energy E_p . To facilitate comparison, the low-temperature data are included in the high-temperature data as solid lines. The spectra are normalized to equal intensity. Obviously, there is no temperature-dependent energetic shift of the APS lines for Fe and Ni, and nor do the line shapes change. In addition, no change of the APS intensity ratio Fe/Ni was detected. As a consequence, we can conclude that no significant segregation of either Fe or Ni onto the surface at high temperatures takes place. We also performed AES measurements of the more surface-sensitive signals of Fe and Ni at 47 and 61 eV, respectively, before and after a heating cycle. The intensity ratio of the two lines did not change within an estimated error of $\pm 6\%$. This result excludes the possibility of an irreversible segregation of one of the two elements.

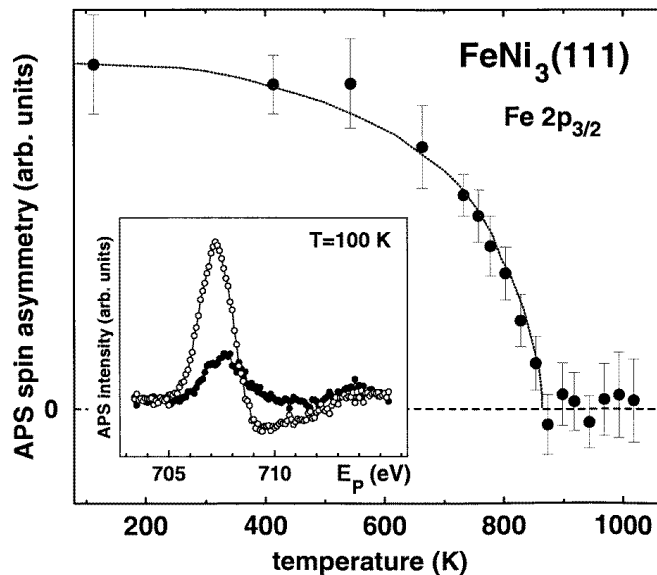


Figure 2. The temperature-dependent spin asymmetry $A = (I_{\uparrow} - I_{\downarrow}) / (I_{\uparrow} + I_{\downarrow})$ of the Fe $2p_{3/2}$ APS signal for $\text{FeNi}_3(111)$. The solid line represents the bulk magnetization of FeNi_3 rescaled to fit the spin-asymmetry data. The low-temperature spin-resolved APS data are shown in the inset. Filled and open circles represent the APS intensities for spin-up (majority) and spin-down (minority) electron excitation, respectively.

The temperature behaviour of the magnetization of the two components within the alloy FeNi_3 was followed by means of spin-resolved APS. Measurements for Fe and Ni at $T = 100$ K are presented in the insets of figures 2 and 3. Filled and open circles represent the APS intensities I_{\uparrow} and I_{\downarrow} for spin-up (majority) and spin-down (minority) electron excitation, respectively. For a detailed discussion of these data and a comparison with theoretical results, the reader is referred to the literature [19]. The spin asymmetry defined as $A = (I_{\uparrow} - I_{\downarrow}) / (I_{\uparrow} + I_{\downarrow})$ serves as a measure of the surface magnetization at the Fe and Ni sites. Since the APS signal of these 3d metals can be described as a matrix-element-weighted self-convolution of the density of empty states [17, 19, 23], the relation between the spin asymmetry and the surface magnetization is not clear beforehand. At least, the spin asymmetry must vanish at the same temperature at which the long-range magnetic order is lost because, at this point, the spin asymmetry in the density of states disappears. Previous studies on Fe, Ni [24], and Fe/Cu(001) [25] essentially suggest a direct proportionality between the spin asymmetry and the surface magnetization, which is supported by our data.

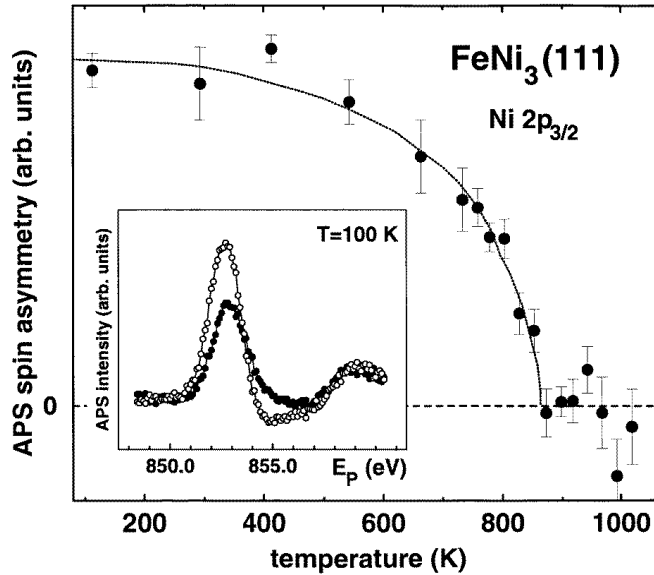


Figure 3. The temperature-dependent spin asymmetry of the Ni $2p_{3/2}$ APS signal for FeNi₃(111). See also the caption to figure 2.

Spin-asymmetry data for the Fe and Ni APS signals from FeNi₃ are shown in figures 2 and 3 as functions of the temperature. For the purposes of comparison, the bulk magnetization curve $M_{\text{bulk}}(T)$ of FeNi₃ [26], rescaled to fit the spin-asymmetry data, is included in figures 2 and 3 as solid lines. We know from figure 1 that the line shapes do not change as a function of the temperature. Furthermore, we found that the values for A do not depend critically on whether they are deduced from the peak maxima or from the integral peak intensities. Therefore, we have restricted the spin-asymmetry measurements to a two-point measurement: one point is within the background at an energy well below the peak energy and one is at the peak position. In addition, we increased V_{p-p} to 3.7 eV to get a better signal-to-background ratio. By doing this, we accepted somewhat lower values for A , which has, however, no influence on the temperature behaviour $A(T)$. Under the conditions described, increasing the modulation voltage only improves the signal-to-background ratio and thereby reduces the measuring time without losing information.

A short measuring time turned out to be important because of the segregation of sulphur to the surface. The crystal was held at high temperatures for only a few minutes, to keep the segregation to a minimum. The temperature-dependent data were obtained by increasing the temperature stepwise to over 1000 K and subsequently decreasing it back stepwise to the starting value. At each temperature value, within a few minutes, A was measured several times. The data from several temperature cycles were accumulated to improve the statistics. The data points and error bars shown in figures 2 and 3 give the mean values plus or minus one standard deviation for all of the data obtained at a given temperature for several heating and cooling cycles. After a heating cycle had been completed, the sulphur contamination at the surface was found to be less than 7%. A comparison of $A(T)$ data taken while the temperature was increased with data obtained while decreasing the temperature exhibited only deviations within the statistical scatter. In particular, no influence of the sulphur segregation on the spin asymmetry was detected.

4. Discussion

The first issue that we want to address is the compositional order–disorder phase transition. In our measurements, the most sensitive indicator is the spin asymmetry. The low-temperature value of A was found to be unchanged whether we measured the supposedly ordered or supposedly disordered state. The latter was prepared by heating the sample to temperatures higher than the transition temperature and then quickly cooling it down to 100 K. In addition, for the temperature cycle described, which starts supposedly in the ordered state, $A(T)$ did not show any deviation from the normal magnetization behaviour as shown in figures 2 and 3. Moreover, no difference was detected for measurements made during fast and slow cooling, which should result in a less and a more ordered crystal, respectively. The spin asymmetry of the APS signal from the magnetically saturated sample was unchanged, whether or not an external field had been applied during the heating and cooling procedures. Nor did the shape of the APS lines change. In summary, no experimental evidence of an order–disorder phase transition was detected in spin-resolved APS for FeNi₃(111) within a probing depth of about six atomic layers.

Experimental evidence of structural disorder at the surface was found after sputtering without annealing. The spin asymmetry decreased by 5% and the second APS peak several eV above the main line was slightly reduced. This structure is sensitive to long-range structural order [27], which is disturbed by sputtering. The compositional order–disorder transition, however, does not change the symmetry of the atomic sites, regardless of their chemical identity, and, therefore, is not expected to be visible in a substantially modified second-peak intensity.

APS has been shown to be sensitive to next-nearest neighbours as demonstrated in our comparative study on Fe and Ni as elements and in the compound FeNi₃ [19]. Therefore, one might expect the order–disorder phase transition to show up in APS. Since this is not the case, we come to the following alternative conclusions as regards the FeNi₃(111) surface.

(i) We cannot detect the phase transition because the differences in the local densities of states between the ordered and disordered state are too small.

(ii) The region sampled does not undergo this transition in the temperature range of the test. At the surface, the number of next-nearest neighbours and the mobility of the atoms is certainly different to within the bulk. Unfortunately, no experimental study on the stoichiometry of the FeNi₃(111) surface is available so far. This study is not an easy enterprise owing to the almost equal scattering properties of the two elements. One should also keep in mind that the cleaning procedure of sputtering and annealing may also have an influence on the compositional order at the surface.

The second point of interest is the magnetic phase transition. From the data in figures 2 and 3 we deduce the following.

(i) The temperature behaviour $A(T)$ is equivalent for Fe and Ni within the compound.

(ii) For both Fe and Ni, $A(T)$ follows the bulk magnetization and vanishes at the bulk Curie temperature T_C^{bulk} . The temperature behaviour of the surface magnetization within the probing depth of APS does not show deviations from the temperature behaviour of the bulk. This result is not surprising. Even investigations with a smaller probing depth of a Ni surface arrived at the same conclusion [28].

(iii) No evidence was found for exceptional properties of the surface. As seen from figures 2 and 3, special care was taken for the temperature range above T_C^{bulk} , where a non-vanishing spin asymmetry was previously reported [15]. In [15], however, the sample

was prepared in a quite different way. For several hours, cycles of sample annealing in an oxygen atmosphere and flashing were used as the cleaning procedure. Perhaps this resulted in a specific, but not identified, iron oxide structure.

Our results are at variance with reference [15], where an enhanced surface Curie temperature of about 1050 K combined with an antiferromagnetic coupling at the (111) surface of FeNi₃ was found. Above T_C^{bulk} the spin asymmetry observed by Mamaev *et al* reaches values as high as were reached below T_C^{bulk} at about 600 K. Our results, however, cannot be directly compared with the results of reference [15] as far as surface phenomena are concerned. Due to the electron energy of 58 eV being used there, the probing depth is only about two atomic layers, which is three times smaller than in our experiment. As a consequence, in the case of a magnetic surface on top of a non-magnetic bulk, our spin-asymmetry signal will be smaller than in the experiment of reference [15]. The expected difference between the two spin-asymmetry data sets owing to the different surface sensitivities of the two techniques depends strongly on the thickness of the magnetically active surface region. The thinner the magnetic region, the larger the difference. On the assumption of only one atomic layer with exceptional magnetic properties, we can estimate a spin asymmetry of at least 10% of the low-temperature value in our data for the temperature region above T_C^{bulk} in order to be consistent with the published data. Even this smallest possible value is beyond the error margins of our experiment.

We also made measurements for an oxidized FeNi₃(111) surface after heating the surface for 20 minutes in a 1×10^{-5} Pa O₂ atmosphere at a sample temperature of about 1000 K. In agreement with an earlier study on polycrystalline FeNi₃ [14] we observed an enrichment of Fe at the surface, but again no magnetic signal above T_C^{bulk} . Further heating of the oxidized surface in ultra-high vacuum leads to a segregation of sulphur, monitored via the AES signal of sulphur. As a result of this, the AES signal of oxygen is reduced and the original Fe/Ni ratio is recovered.

Furthermore, one may consider a temperature-dependent compositional change at the surface as a possible origin of a magnetic surface phase different from the bulk. Our element-specific APS results in combination with the AES study described in section 3 provide no evidence of such an effect.

In summary, the FeNi₃(111) surface, prepared in various ways as described above, did not show any exceptional surface magnetic properties in spin-resolved APS. Future experiments should focus on the compositional order at the surface and its dependence on preparation conditions. These studies should be combined with magnetic measurements to find a relationship between the compositional order and the magnetic properties.

A further result of our study on the temperature-dependent magnetization of FeNi₃(111) is the confirmed proportionality of the spin asymmetry $A(T)$ from APS measurements and the magnetization $M(T)$. All of the results obtained prove APS to be well suited to element-specific magnetization studies of multi-component systems such as alloys and layered structures.

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References

- [1] Cullity B D 1972 *Introduction to Magnetic Materials* (Reading, MA: Addison-Wesley)
- [2] Wakelin R J and Yates E L 1953 *Proc. Phys. Soc. B* **66** 221
- [3] Cable J W and Wollan E O 1973 *Phys. Rev. B* **7** 2005
- [4] Calvayrac Y and Fayard M 1973 *Phys. Status Solidi a* **17** 407
- [5] Drijver J W, van der Woude F and Radelaar S 1975 *Phys. Rev. Lett.* **34** 1026
- [6] Drijver J W, van der Woude F and Radelaar S 1977 *Phys. Rev. B* **16** 985
- [7] Drijver J W, van der Woude F and Radelaar S 1977 *Phys. Rev. B* **16** 993
- [8] Cranshaw T E 1987 *J. Phys. E: Sci. Instrum.* **17** 967
- [9] Staunton J B, Johnson D D and Györffy B L 1987 *J. Appl. Phys.* **61** 3693
- [10] Staunton J B, Johnson D D, Györffy B L and Walden C 1990 *Phil. Mag. B* **106** 773
- [11] Johnson D D, Pinski F J, Staunton J B, Györffy B L and Stocks G M 1990 *Physical Metallurgy of Controlled Expansion Invar-Type Alloys* ed K C Russell and D F Smith (Washington, DC: The Minerals, Metals and Materials Society) p 3
- [12] Dang M-Z and Rancourt D G 1996 *Phys. Rev. B* **53** 2291
- [13] Hague C F, Källne E, Mariot J M, Dufour G, Karnatak R C and Bonnelle C 1976 *J. Phys. F: Met. Phys.* **6** 899
- [14] Wandelt K and Ertl G 1976 *J. Phys. F: Met. Phys.* **6** 1607
- [15] Wandelt K and Ertl G 1976 *Surf. Sci.* **55** 403
- [16] Mamaev Yu A, Petrov V N and Starovoitov S A 1987 *Sov. Tech. Phys. Lett.* **13** 642
- [17] Kirschner J 1984 *Solid State Commun.* **49** 39
- [18] Ertl K, Vonbank M, Dose V and Noffke J 1993 *Solid State Commun.* **88** 557
- [19] Detzel Th, Vonbank M, Donath M and Dose V 1995 *J. Magn. Magn. Mater.* **147** L1
- [20] Detzel Th, Memmel N, Vonbank M, Donath M and Dose V 1995 *Phys. Low-Dimens. Struct.* **8+9** 1
- [21] Reinmuth J, Passek F, Petrov V N, Donath M, Popescu V and Ebert H 1997 *Phys. Rev. B* **56** 12893
- [22] Park R L and Houston J E 1972 *Phys. Rev. B* **6** 1073
- [23] Kolac U, Donath M, Ertl K, Liebl H and Dose V 1988 *Rev. Sci. Instrum.* **59** 1931
- [24] Rangelov G, Ertl K, Passek F, Vonbank M, Bassen S, Reinmuth J, Donath M and Dose V 1998 *J. Vac. Sci. Technol. A* at press
- [25] Ebert H and Popescu V 1997 *Phys. Rev. B* **56** 12884
- [26] Vonbank M 1992 *Doctoral Thesis* Technische Universität Wien
- [27] Detzel Th, Vonbank M, Donath M, Memmel N and Dose V 1996 *J. Magn. Magn. Mater.* **152** 287
- [28] Crangle J and Hallam G C 1963 *Proc. R. Soc. A* **272** 119
- [29] Dose V, Drube R and Härtl A 1986 *Solid State Commun.* **57** 273
- [30] von der Linden W, Donath M and Dose V 1993 *Phys. Rev. Lett.* **71** 899