

## INTERRELATION BETWEEN MAGNETIC PROPERTIES AND PHASE COMPOSITION FOR THE SURFACE OF (111) FACE OF FeNi<sub>3</sub> PERMALLOY

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The investigation of the influence of the atomic structure and the element and phase compositions on the superficial magnetic properties of (111) face of FeNi<sub>3</sub> alloy has been carried out. It is found that the thermostimulated segregative enrichment of a near-surface layer by iron gives rise to the appearance of a premature atomic disorder and martensitic structural phase transformations  $\gamma \rightleftharpoons (\alpha + \gamma)$  in this layer. As a result of the tight relation of the spontaneous magnetization to the phase composition of a near-surface layer, a complicated character of the temperature dependence of the spin-exchange asymmetry of the scattering for a beam of spin-polarized low-energy electrons is observed. So, as the temperature of a specimen grows starting from room temperature, the spin-exchange asymmetry of the scattering, which reflects the behavior of the spontaneous magnetization of a near-surface layer, changes the sign twice and eventually disappears near the Curie temperature of  $\alpha$ -iron. It is established that the double change in the sign of the spin-exchange asymmetry of the scattering originates from the existence of the antiferromagnetic coupling between the magnetic moments of precipitates of the  $\alpha$ -phase and those of the  $\gamma$ -phase of FeNi<sub>3</sub> permalloy. It is found that the amount of precipitates of the  $\alpha$ -phase segregated in the near-surface layer is changed non-monotonously with temperature and reaches the peak values near the points of order-disorder or ferromagnet-paramagnet phase transitions characteristic of the bulk FeNi<sub>3</sub> alloy.

### 1. Introduction

As a general rule, the magnetic properties of the surface of a solid essentially differ from those of a solid bulk. First of all, this is caused by the breakdown of the translational invariance at the interface with vacuum and the difference in bonding forces acting between the nearest-neighbor atoms or their magnetic moments at the surface and inside the matter. At the same time, a possible discrepancy in the element and phase compositions between the near-surface layer and the bulk plays an important role for binary alloys. For the atomically clean surfaces, the influence of these factors gives rise to the different temperature dependences of the surface and bulk magnetizations, the appearance of

purely superficial magnetic phase transitions, a change in the type of a surface magnetic ordering in comparison with the bulk one, as well as to a modification of the character of the spin-exchange interaction between the magnetic moments of the near-surface and internal atoms.

For example, in works [6–8], the different kinds of the temperature behavior were observed for the surface and bulk magnetizations of Ni (001) and (110). At the same time, the Curie point for the nickel surface turned out to equal that for the bulk with a precision of  $\pm 4$  K. A similar picture was observed for the surfaces of Fe (100) and (110) [9–11] and also for amorphous ferromagnets Fe<sub>40</sub>Ni<sub>40</sub>B<sub>20</sub> and Fe<sub>81.5</sub>Ni<sub>14.5</sub>Si<sub>4</sub> [12,13]. The surface magnetization almost linearly decreased with increase in temperature and disappeared at a temperature which was close to the bulk Curie temperature  $T_{Cb}$ . In work [14], by the method of sliding inelastic scattering of deuterons with the capture of surface electrons, the surface ferromagnetism was revealed for a V (100) single crystal which is a paramagnet in the bulk. The value of the Curie point  $T_{Cs}$  for the (100) surface face of vanadium was found to equal  $\simeq 540$  K. A ferromagnetic phase transition was also observed at the surface of Cr (100) [15,16] by spin-resolved photoelectron spectroscopy. A higher value, in comparison to the bulk, of the Curie point was also observed for the surface of Gd (0001) films deposited on a tungsten substrate [17–19]. In addition, the presence of the antiferromagnetic coupling between the spins of near-surface and internal atoms was revealed in these works. In recent years, the experimental investigation of superficial magnetic phase transitions has repeatedly attracted the attention of researchers, and, to date, a number of reports on the continuous rearrangement of spins on a free surface is available [20].

The methods of spin-polarized electron spectroscopy, especially spin-polarized low-energy electron diffraction

(SPLEED) with electron energies  $E_0 = 10 \div 200$  eV, make it possible to obtain information on the magnetic properties of the near-surface region of single crystals which includes several outer atomic layers [21]. The SPLEED method plays such an important role in the study of the magnetism of two-dimensional systems, as the neutron diffraction method does in the investigation of magnetic properties of the bulk. It is especially noteworthy that SPLEED is exceptionally sensitive to the magnetic properties of a surface. A probing depth is determined, as a rule, by a free path for the inelastic scattering,  $\lambda = \lambda(E_0)$  [22]. For example, if the cross-section of a probing beam is  $\sim 1$  cm<sup>2</sup> and the free path  $\lambda \approx 10$  Å, the volume of a material subjected to the exposition equals  $10^{-9}$  cm<sup>3</sup>. It is not possible, in principle, to detect the signal from a specimen of such dimensions with the use of any ordinary magnetometer. It is this circumstance that lies in the basis of the exceptional informativity of SPLEED for the investigation of the surface magnetism and the magnetism of thin films.

The aim of this work is to study the effect of elemental and phase compositions on the magnetic properties of the thinnest near-surface layer of a FeNi<sub>3</sub> (111) single crystal by means of SPLEED. At present, it is precisely known that there is a tight interrelation between the bulk magnetic properties of steels and alloys, on the one hand, and the elemental and phase compositions of these materials, on the other hand [23]. Moreover, the segregation profiles for iron and a degree of long-range order are experimentally studied for FeNi<sub>3</sub> (111) [24,25]. It is these facts that favor the statement of the problem for this work.

## 2. Experimental Technique

The SPLEED method is one of the methods of spin-resolved spectroscopy of elastically reflected electrons. In our experiments on the investigation of the surface magnetism, the scattering geometry for a beam of polarized electrons was chosen as shown in Fig. 1. The beam of primary electrons with a polarization  $\vec{P}_0$  and energy  $E_0$  falls on the specimen surface at an angle  $\theta = 13^\circ$ . The polarization of the primary beam is either parallel or antiparallel to the normal  $\vec{n}$  of a scattering plane:

$$\vec{n} = [\vec{k}, \vec{k}'] / |[\vec{k}, \vec{k}']|, \quad (1)$$

where  $\vec{k}$  and  $\vec{k}'$  are the wave vectors of incident and scattered electrons, respectively. On the study of (111) face of FeNi<sub>3</sub>, the scattering plane coincided with (110)

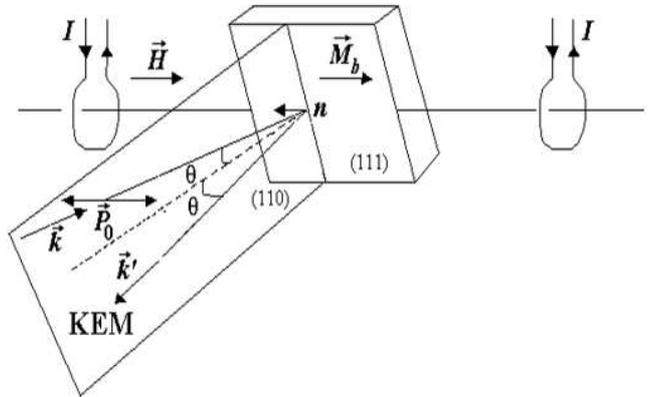


Fig. 1. Geometry of the scattering of a beam of spin-polarized electrons by a magnetic target

plane of a crystal. The bulk magnetization of a specimen,  $\vec{M}_b$ , was oriented in the direction of the external magnetic field  $\vec{H}$  and was also either parallel or antiparallel to  $\vec{n}$ . The mirror reflex intensity for elastically reflected electrons was recorded in two cases where the polarization  $\vec{P}_0$  was either parallel ( $I^{(+)}$ ) or antiparallel ( $I^{(-)}$ ) to the bulk magnetization. From the values of  $I^{(+)}$  and  $I^{(-)}$ , the corresponding values of the asymmetry of scattering,

$$A^{(\pm)} = \frac{1}{P_0} \frac{I^{(+)}(\pm H) - I^{(-)}(\pm H)}{I^{(+)}(\pm H) + I^{(-)}(\pm H)}, \quad (2)$$

were calculated. It was noted in works [6, 26] that it is possible to separate the contributions to the scattering asymmetries  $A^{(\pm)}$  from spin-orbital and spin-exchange interactions. With a good precision (the error of measurements was about 1%), the spin-orbit asymmetry of scattering ( $A_{SL}$ ), while neglecting the influence of spin-exchange interaction, and the spin-exchange asymmetry of scattering ( $A_{SE}$ ), while neglecting the influence of spin-orbit interaction, are given by the expressions:

$$A_{SL} = (A^{(+)} + A^{(-)})/2, \quad (3)$$

and

$$A_{SE} = (A^{(+)} - A^{(-)})/2. \quad (4)$$

The main point in the interpretation of the SPLEED data is the relation of the spin-exchange asymmetry  $A_{SE}$  to both the surface magnetization  $M_s$  and a change

of magnetic properties when going from the surface deep into the specimen ( $M_s \rightarrow M_b$ ). In the Born approximation, there is a direct proportion between  $A_{SE}$  and  $M_s$  [27]. The dynamic calculations with regard for a multiple scattering result in a more complicated dependence of  $A_{SE}$  on  $M_s$ :

$$A_{SE} \propto \alpha M_s + \beta M_s^3 + \gamma M_s^5 + \dots \quad (5)$$

In a general case, the constants  $\alpha, \beta$ , and  $\gamma$  contain the exchange and Coulomb potentials of scattering [28]. The even degree terms are absent in this series because  $A_{SE}$  should change a sign, by definition, at the magnetization direction reversal. It is shown in work [29] that in the frames of the dynamic theory of low-energy electron diffraction (LEED), the third- and higher order terms in expression (5) can be neglected at temperatures close to the Curie point  $T_{Cs}$ . This follows from a strong increase in the magnetic coherence length as the specimen temperature approaches  $T_{Cs}$ . Thus, within the critical region of temperatures,  $A_{SE}$  is proportional to  $M_s$ , which can be described, according to the theoretical views of work [8], as

$$A_{SE} \sim M_s \sim \left(1 - \frac{T}{T_{Cs}}\right)^{\beta_s}, \quad (6)$$

whereas

$$M_b \sim \left(1 - \frac{T}{T_{Cb}}\right)^{\beta_b}, \quad (7)$$

where  $\beta_s$  and  $\beta_b$  are the critical indices for the surface and bulk magnetizations, respectively. In what follows, we will use these relations for the interpretation of experimental results.

The measurements were carried out with the use of an ultrahigh-vacuum diffractometer of spin-polarized electrons, which operated at a pressure of residual gases not more than  $10^{-10}$  Pa. A heating system made it possible to vary the specimen temperature from room temperature up to 1200 K and to measure it with the use of a chromel-alumel thermocouple with a precision of  $\pm 5$  K. At room temperature, the atomically clean (111) surface of FeNi<sub>3</sub> alloy was not reconstructed, and its cleanness was checked by Auger electron spectroscopy.

A semiconducting photoemitter with a negative electron affinity, namely GaAs doped with phosphorus (GaAs<sub>0.64</sub>P<sub>0.36</sub>), served as a source of a beam of spin-polarized electrons. A primary source of light (the emission was in the range of energies  $h\nu = 1.3 \div 3.6$  eV) was a halogen lamp with the power characteristics

100 W×12 V. The linearly polarized monochromatic light, obtained with the use of a double monochromator, passed through a Glan–Thompson polarizer and a photoelastic quartz modulator. This resulted in the formation of the flux of a circularly polarized light modulated with the frequency  $\omega_0 = 31$  kHz. Under the action of this light flux falling on a photoemitter surface, the spin-polarized electrons arose and then were collimated in a beam with the polarization, whose direction was modulated from  $-\vec{P}_0$  to  $\vec{P}_0$  with the frequency  $\omega_0$ . It is possible with such a modulation of the polarization of a primary electron beam to fix right away two values of the mirror reflex intensity for elastically reflected electrons,  $I^{(\pm)}$ , first at the orientation of magnetic field accepted as “left” ( $-\vec{H}$ ) and then at that accepted as “right” ( $\vec{H}$ ). After the determination of four values of the scattering intensity, both the spin-orbit and spin-exchange asymmetries of scattering can be easily calculated according to formulas (2)–(4).

The scattering intensities  $I^{(\pm)}$  were registered with the use of a channel electron multiplier operating in the pulse counting mode. The degree of polarization  $P_0$  for the primary electron beam reached about 30%. The sensitivity of the measurements of the asymmetry of scattering was near 0.1% in the case where the counting rate of a channel electron multiplier equaled  $3 \times 10^4$  s<sup>-1</sup> and the time of the pulse acquisition was of the order of several minutes. To diminish the influence of spurious magnetic fields, the conditions, which drove the electrons with their energy of near 1 keV to move along the electron-optical system, were created. What is more, all the elements of the system were made from a nonmagnetic stainless steel, and the optical inlet had a separate magnetic screen made from permalloy.

### 3. Experimental Results

Figure 2 shows the dependences of  $A_{SL}$  and  $A_{SE}$  on energy  $E_0$  obtained at room temperature for the range of energies 10–120 eV. For the values of  $E_0$  greater than 120 eV, both the spin-orbit and spin-exchange asymmetries of scattering completely disappear. The peculiarities in these curves are likely to be caused by the influence of the crystal structure of a target. The absolute values for both  $A_{SL}$  and  $A_{SE}$  agree by order of magnitude with those obtained in other experiments [28–30] and with the results of the calculations carried out on the basis of the relativistic theory of LEED for the

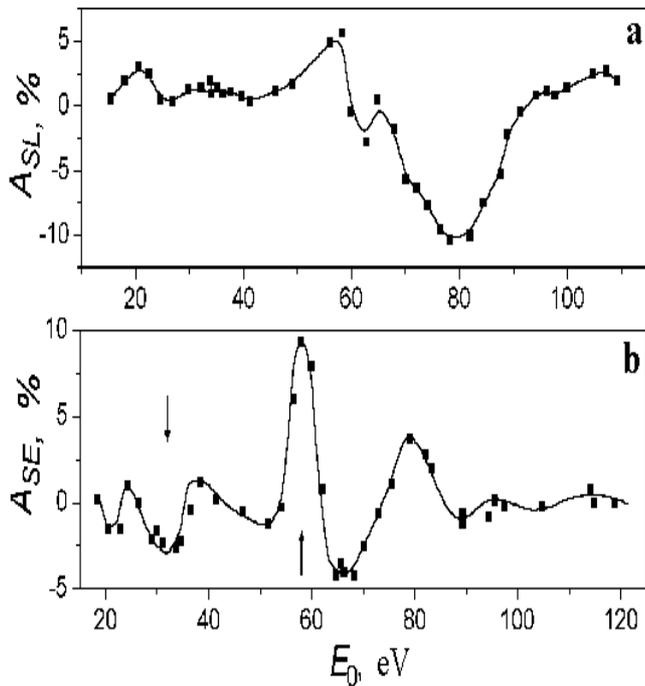


Fig. 2. Energy dependences of the spin-orbital (a) and spin-exchange (b) asymmetries of scattering for FeNi<sub>3</sub> (111). The arrows show the values of energy  $E_0$ , at which the temperature dependence of the spin-exchange asymmetry of scattering  $A_{SE}$  was studied

electrons elastically reflected from the surfaces of transition metals [32]. Moreover, the maximal value of the spin-exchange asymmetry of scattering observed at  $E_0 = 58$  eV is approximately equal to 10%. Such order of magnitude is also characteristic of the polarization of secondary electrons ( $\sim 6\%$  at  $E_0 = 200$  eV) generated as a nonpolarized electron beam falls on polycrystalline permalloy [33].

To verify the magnetic nature of the scattering asymmetry  $A_{SE}$ , its dependence on the magnetizing force  $\vec{H}$  was studied. A typical hysteresis loop is shown in Fig. 3. It should be noted that the spurious influence of the field in the vicinity of a specimen can distort the path of electron motion near the specimen surface, which can result in the appearance of the instrumental asymmetry, whose presence can be detected at the inversion of field  $\vec{H}$ . The influence of such “asymmetry” should lead to an increase in  $A_{SE}$  with increase in the external field. However, as is seen from Fig. 3, the  $A_{SE}(H)$  dependence saturates at 1 Oe. This means that the value of  $A_{SE}$ , obtained by us in measurements, originates just from the exchange interaction between the polarized beam and the electrons of a magnetic target. The coercivity

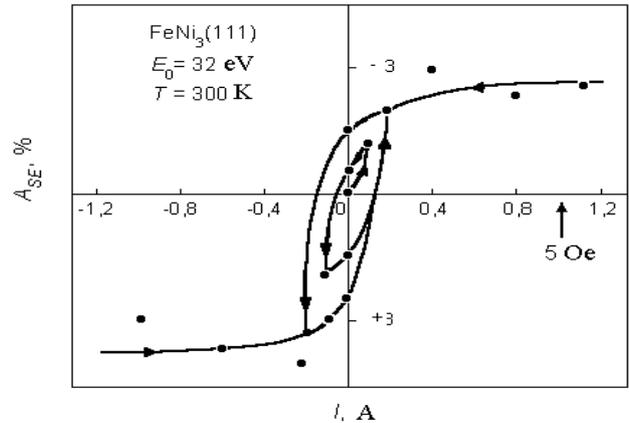


Fig. 3. Hysteresis loop for the spin-exchange asymmetry of scattering as a function of the electric current in magnet coils

determined from the hysteresis loop turns out to be 0.75 Oe for the surface of permalloy. The coercivity for bulk FeNi<sub>3</sub> alloy equals 0.54 Oe [34].

The main aim of this work is the study of the magnetic properties of the surface of (111) face of FeNi<sub>3</sub> alloy, basing on the analysis of the temperature dependence of  $A_{SE}$ . The experiments were performed in the temperature range 300–1100 K at two values of energy, namely,  $E_0 = 32$  and 58 eV. In the course of measurements, a possible shift of the chosen extremum of  $A_{SE}$  along the energy axis, which can arise from the thermal expansion of a crystal, was taken into account. The temperature dependences of the spin-exchange asymmetry of scattering  $A_{SE} = A_{SE}(T)$  were obtained by measurements in the saturation field and are shown in Fig. 4. We note that the  $A_{SE}(T)$  dependences obtained at  $E_0 = 32$  and 58 eV have a complex character but their peculiar features are similar to each other (see Figs. 4a,b). So, as the temperature increases from room one, the spin-exchange asymmetry of scattering first decreases, then changes a sign at  $T \approx 740$  K and achieves a minimum at a temperature which is close to the point of the order-disorder phase transition for FeNi<sub>3</sub> alloy ( $T_{Ob}^{(\gamma)} = 776$  K). After this, it sharply rises, repeatedly changes a sign in a range of temperatures close to the Curie point of bulk FeNi<sub>3</sub> alloy ( $T_{Cb}^{(\gamma)} = 863$  K), and goes to zero near the Curie point of bulk  $\alpha$ -iron ( $T_{Cb}^{(\alpha)} = 1043$  K).

#### 4. Discussion of Results

Consider, in more details, the reasons for such complicated character of the  $A_{SE}$  vs  $T$  dependences.

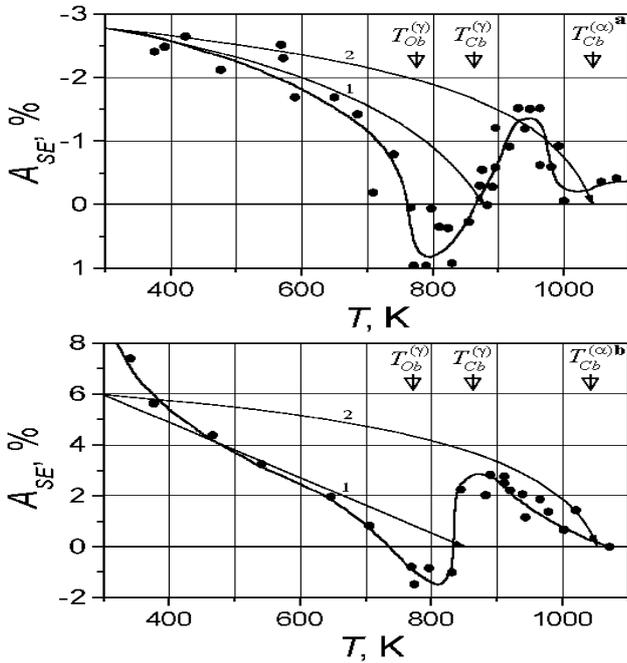


Fig. 4. Temperature dependences of the spin-exchange asymmetry of scattering measured for two energies of the primary electron beam  $E_0$ : 32 (a) and 58 eV (b)

First of all, we calculate the mean free path for inelastic electron scattering. According to the results of work [22], it can be found by the relation

$$\lambda(E_0) = \frac{1}{2} \left[ \frac{2470}{\rho_m^{1/3} E_0^2} + 0.41 \left( \frac{A_m}{6.02 \rho_m} \right)^{1/2} E_0^{1/2} \right]. \quad (8)$$

Here,  $\lambda(E_0)$  is measured in Å, when the target density  $\rho_m$  is taken in g/cm<sup>3</sup>, the average atomic mass  $A_m$  of the target – in atomic mass units (amu), and the energy of the primary electron beam  $E_0$  – in eV. Formula (8) accounts also for the fact that the primary spin-polarized electrons pass a double distance in the process of elastic diffraction: first, from vacuum inside a crystal and then, after the backscattering, from the inside of the crystal to vacuum. In our case,  $\rho_m = 8.645$  g/cm<sup>3</sup> and  $A_m = 57.979$  amu. As a result, the values of the mean free path calculated for  $E_0 = 32$  and 58 eV, are 1.813 and 1.828 Å, respectively. The obtained values are close to each other, and their examination on the basis of the assumption that the intensity of a primary electron beam decays exponentially with a depth shows that, in both cases, the near-surface layer contributes ~ 70% to the experimentally measured spin-exchange asymmetry of scattering. Thus, the double change in the  $A_{SE}$  sign that we observed as the temperature was increased

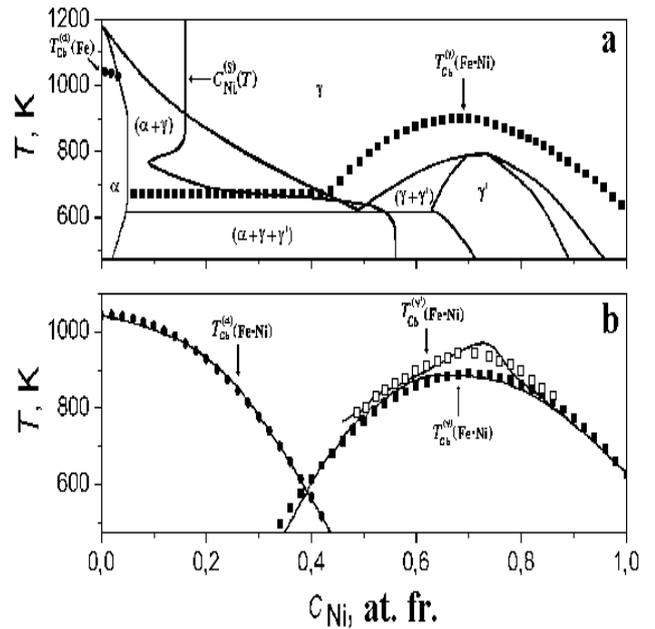


Fig. 5. General (a) and magnetic (b) volume phase diagrams for the Fe–Ni system

is exclusively superficial. It should be noted that, in the case of the diffraction of spin-polarized electrons on ferromagnetic targets, there exists also spin dependence of the mean free path  $\lambda^{(\pm)}(E_0)$ . However, according to the results of paper [26], this dependence is weak.

In a general phase diagram of the Fe–Ni system shown in Fig. 5a, we chart the temperature dependence of the concentration of nickel in a surface layer  $C_{Ni}^{(s)}$  measured in [24] by means of ionization spectroscopy with the subsequent employment of the technique of nondestructive layer-by-layer analysis. It follows from Fig. 5a that, according to the phase diagram, the composition of the near-surface layer falls into the eutectic three-phase region  $(\alpha + \gamma + \gamma')$  and then shifts to the two-phase region  $(\gamma + \gamma')$  with increase in the temperature. However, it is most likely that for the temperatures ranging from 300 to 650 K, the surface layer always consists of a mixture of two phases  $(\gamma + \gamma')$  due to the influence of the ordering in the bulk and the near-surface region.

At temperatures higher than ~650 K, the segregation of precipitates of the  $\alpha$ -phase occurs which goes according to the martensitic (non-diffusive) shear mechanism [34–36]. At the same time, according to the results of paper [25], the long-range atomic order in a near-surface region also begins to sharply deteriorate at

temperatures exceeding 650 K. It turns out that, due to the enhancement of the surface segregation of iron, the outer near-surface layers becomes disordered with the signature of the second-order phase transition at a temperature which is about 120 K lower than the point of the order-disorder phase transition for the bulk FeNi<sub>3</sub>. Thus, it can be stated that, in the near-surface layers, the crossover from a phase transition of the type of order-disorder to that of the shear type is observed. However, the behavior of the temperature dependences of  $A_{SE}$  can only be explained completely if one assume that then a strong enrichment of precipitates of the  $\alpha$ -phase by iron occurs under the influence of diffusion. Moreover, the antiferromagnetic character of the coupling between the magnetic moments of iron atoms in precipitates of the  $\alpha$ -phase and those in the  $\gamma$ -phase of permalloy is observed.

The Curie point for the surface of the FeNi<sub>3</sub> (111) alloy just corresponds to the Curie point of  $\alpha$ -iron. For this reason, the formed precipitates of the  $\alpha$ -phase are not single-layered but contain a great number of atomic layers. The expression describing the dependence of the Curie temperature on the number  $L$  of layers forming a precipitate has the form [37]:

$$T_{CL}^{(\alpha)} = (T_{Cb}^{(\alpha)}/2)[1 + \cos(\pi/(L+1))]. \quad (9)$$

It turns out that the value which is close to the bulk Curie point of  $\alpha$ -iron is only achieved if  $L \geq 6$ .

We carry out the further analysis of the  $A_{SE}$  vs  $T$  dependences under the assumption that the spin-exchange asymmetry of scattering is directly proportional to the surface spontaneous magnetization. At first, as the temperature rises from 300 to  $\sim 650$  K, the spin-exchange asymmetry of scattering decreases almost linearly with increase in the temperature (see Fig. 4), which is caused by a deterioration of the long-range order characteristic of spins of the ferromagnetic surface. The further sharp drop and the change in the sign of  $A_{SE}$  are brought about by the segregation of precipitates of the  $\alpha$ -phase which consist mainly of iron atoms and display the antiferromagnetic interaction with the spins of atoms of the  $\gamma$ -phase of permalloy. The change in the sign of the spin-exchange asymmetry of scattering implies that, at a further heating of the specimen, the amount of precipitates of the  $\alpha$ -phase continues to grow. At  $T < T_{Cb}^{(\gamma)}$ , the exchange interaction for the atomic spins exceeds by far the external magnetic field  $\vec{H}$  applied to the specimen. For this reason, the antiparallel orientation of the spontaneous magnetizations of the  $\gamma$ - and  $\alpha$ -phases persists up to the bulk Curie temperature for FeNi<sub>3</sub> alloy. Near  $T_{Cb}^{(\gamma)}$ , a reorientation of the

spontaneous magnetization of precipitates of the  $\alpha$ -phase in the direction of the field  $\vec{H}$  occurs, which gives rise to the repeated jump-like change in the  $A_{SE}$  sign. As the specimen is heated through  $T_{Cb}^{(\alpha)}$ , the spin-exchange asymmetry of scattering practically disappears, due to the transition of precipitates of the  $\alpha$ -phase into the paramagnetic state (see Fig. 4).

The diameter of a primary electron beam is sufficiently large and equals about 1 mm. Thus, for the spin-exchange asymmetry of scattering we measure, the additivity principle,

$$A_{SE}(T) \sim C_s^{(\gamma)} M_s^{(\gamma)} - C_s^{(\alpha)} M_s^{(\alpha)}, \quad (10)$$

is valid. Here,  $C_s^{(\gamma)}$  and  $C_s^{(\alpha)}$  are the amounts of the  $\gamma$ - and  $\alpha$ -phases, respectively, in the near-surface region,  $M_s^{(\gamma)}$  and  $M_s^{(\alpha)}$  are the corresponding spontaneous magnetizations. The minus sign arises due to the presence of the antiferromagnetic coupling between the magnetic moments in the surface precipitates of the  $\alpha$ -phase and those in the  $\gamma$ -phase of bulk FeNi<sub>3</sub> permalloy. We can derive the expressions which allow one to carry out the magnetic phase analysis for the surface of (111) face of FeNi<sub>3</sub> alloy. In the case where the changes in the eutectic phase can be described by the formula [35]

$$[\gamma + \gamma'] \iff [(\alpha - \text{Fe}) + (\gamma - \text{FeNi}_3)], \quad (11)$$

the above expressions take the form

$$C_s^{(\alpha)} = 1 - \frac{\mu_{\text{FeNi}_3}^{(\gamma)} (A_{SE}(T)/A_{SE}^{(*)}) + \mu_{\text{Fe}}^{(\alpha)} m_s^{(\alpha)}}{\mu_{\text{FeNi}_3}^{(\gamma)} m_s^{(\gamma)} + \mu_{\text{Fe}}^{(\alpha)} m_s^{(\alpha)}}, \quad (12)$$

$$650 < T < 863 \text{ K},$$

$$C_s^{(\alpha)} = \frac{\mu_{\text{FeNi}_3}^{(\gamma)} (A_{SE}(T)/A_{SE}^{(*)})}{\mu_{\text{Fe}}^{(\alpha)} m_s^{(\alpha)}}, \quad (13)$$

$$863 < T < 1043 \text{ K}.$$

Here,  $A_{SE}^{(*)}$  are the normalization coefficients,  $m_s^{(\gamma)}$  and  $m_s^{(\alpha)}$  are curves 1 and 2 shown in Figs. 4a,b,  $\mu_{\text{FeNi}_3}^{(\gamma)}$  and  $\mu_{\text{Fe}}^{(\alpha)}$  are the magnetic moments of FeNi<sub>3</sub> alloy and  $\alpha$ -iron which equal 1.15  $\mu_B$  and 2, 2  $\mu_B$ , respectively, where  $\mu_B$  is the Bohr magneton.

The results of the magnetic phase analysis for the surface of (111) face of FeNi<sub>3</sub> alloy are shown in Figs. 6,a,b. It was revealed that the amount of precipitates of the  $\alpha$ -phase segregated in the near-surface region is a non-monotonous function of temperature and reaches the peak values in the vicinity of the temperatures which

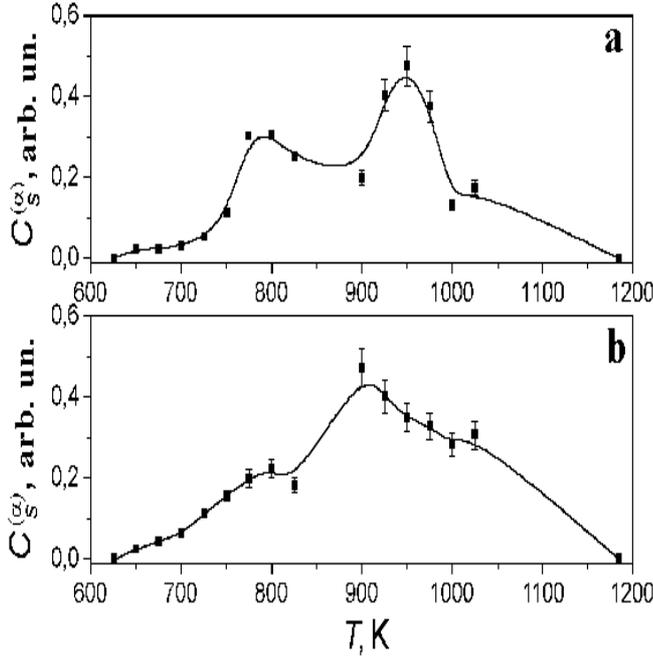


Fig. 6. Results of the magnetic phase analysis for the surface of the FeNi<sub>3</sub> (111) alloy. The data were obtained from the temperature dependences of the spin-exchange asymmetry of scattering measured for two values of the primary electron beam  $E_0$ : 32 (a) and 58 eV (b)

are close to the points of the order-disorder and ferromagnet-paramagnet phase transitions for bulk FeNi<sub>3</sub> alloy. It also follows from Fig. 6 that at most a half of the relative fraction of the matter in the near-surface region undergoes the martensitic structural phase transition.

The fundamental possibility that the antiferromagnetic coupling can exist in the  $\gamma$ -phase of Fe–Ni alloys follows from the optimization of the exchange interaction parameters carried out according to the data of the bulk magnetic phase diagram (solid squares in Fig. 5, b). These data were obtained with the use of the expressions for the Neel and Curie points taken from [38, 39]:

$$T_{Nb}^{(\gamma)} = (Z/6k)(C_{Fe}^2 J_{FeFe}^{(\gamma)} + C_{Ni}^2 J_{NiNi}^{(\gamma)} + 2C_{Fe}C_{Ni}J_{FeNi}^{(\gamma)}),$$

$$0 < C_{Ni} < 0.156, \quad (14)$$

$$T_{Cb}^{(\gamma)} = (Z/2k)(C_{Fe}^2 J_{FeFe}^{(\gamma)} + C_{Ni}^2 J_{NiNi}^{(\gamma)} + 2C_{Fe}C_{Ni}J_{FeNi}^{(\gamma)}),$$

$$0.156 < C_{Ni} < 1, \quad (15)$$

where  $Z = 12$  is the coordination number for bulk  $\gamma$ -alloys,  $C_{Fe}$  and  $C_{Ni}$  are the bulk concentrations of iron and nickel, respectively, in Fe–Ni alloy,  $J_{FeFe}^{(\gamma)} = -98.33$ ,  $J_{NiNi}^{(\gamma)} = 104.58$ , and  $J_{FeNi}^{(\gamma)} = 252$  are the parameters of exchange interaction measured in Kelvins for the spins of the corresponding pairs of atoms. Thus, in the  $\gamma$ -alloys of Fe–Ni (austenites), the exchange interaction for the Fe–Fe pairs of atoms is antiferromagnetic. At the same time, the austenite alloys containing less than 15.6 bulk percents of nickel are antiferromagnets.  $\gamma$ -iron is also antiferromagnetic with the Neel point  $T_{Nb}^{(\gamma)}(Fe) \simeq 69$  K [40].

Optimization of the parameters of exchange interaction for ordered  $\gamma'$ -alloys of Fe–Ni (open squares in Fig. 5) was carried out basing on the expression taken from works [38, 39]:

$$T_{Cb}^{(\gamma')} = (Z/2k)(C_{Fe}^2 J_{FeFe}^{(\gamma)} + C_{Ni}^2 J_{NiNi}^{(\gamma)} + 2C_{Fe}C_{Ni}J_{FeNi}^{(\gamma)} + J(\eta_m/4)), \quad 0.47 < C_{Ni} < 0.86. \quad (16)$$

Here,

$$\eta_m = \begin{cases} (1 - C_{Ni})/(1 - C_{Ni}^{(m)}), & C_{Ni}^{(m)} \leq C_{Ni} \leq 0.86, \\ C_{Ni}/C_{Ni}^{(m)}, & 0.47 \leq C_{Ni} \leq C_{Ni}^{(m)} \end{cases}$$

is the degree of long-range order for the state most ordered of all possible states of the  $\gamma'$ -alloy of Fe–Ni for a fixed  $C_{Ni}$ ,  $C_{Ni}^{(m)} = 0.72$  is the alloy concentration, at which the maximal degree of long-range atomic order is achieved,  $J = 155.13$  K is the magnetic exchange energy of the system. Thus, in the ordered  $\gamma'$ -alloys of Fe–Ni, the antiferromagnetic character of the exchange interaction for the Fe–Fe pairs of atoms persists.

A similar procedure of the optimization of the parameters of exchange interaction for the martensite  $\alpha$ -alloys of Fe–Ni (solid circles in Fig. 5) was carried out using the expression

$$T_{Cb}^{(\alpha)} = (Z/2k)(C_{Fe}^2 J_{FeFe}^{(\alpha)} + C_{Ni}^2 J_{NiNi}^{(\alpha)} + 2C_{Fe}C_{Ni}J_{FeNi}^{(\alpha)}), \quad 0 < C_{Ni} < 0.438, \quad (17)$$

where  $Z = 8$  is the coordination number for the bulk  $\alpha$ -alloys,  $J_{FeFe}^{(\alpha)} = 260.75$ ,  $J_{NiNi}^{(\alpha)} = -495.1$ , and  $J_{FeNi}^{(\alpha)} = 264.35$  are the exchange interaction parameters measured in Kelvins for the spins of the corresponding pairs of atoms in the martensitic  $\alpha$ -phase. Thus, the

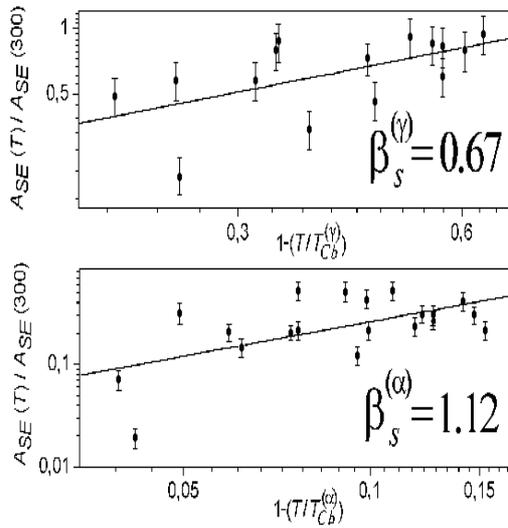


Fig. 7. Logarithmic temperature dependences of the normalized spin-exchange asymmetry of scattering for the  $\gamma$ -phase of FeNi<sub>3</sub> (111) (a) and precipitates of the  $\alpha$ -phase formed in the near-surface region of the alloy (b)

exchange interaction for the Ni–Ni pairs of atoms is antiferromagnetic in the  $\alpha$ -alloys of Fe–Ni. It is appropriate to assume in this respect that, since the magnetic properties of the near-surface region can strongly differ from those of the bulk, it might be possible for precipitates of the  $\alpha$ -phase, enriched with iron, to couple antiferromagnetically with the  $\gamma$ -phase of permalloy. We note that, for Fe–Ni invar alloys, the possibility that antiferromagnetic clusters could be formed in the ferromagnetic matrix was also noted in work [41]. In addition, an important property of the thin iron layers separated by a chromium spacer was revealed in paper [42] by means of SPLEED. It was shown that, at certain thicknesses of the iron and chromium layers, the coupling between the layers becomes antiferromagnetic. All these experimental data confirm the physical validity of our assumption about the antiferromagnetic coupling between the magnetic moments in precipitates of the  $\alpha$ -phase and those in the  $\gamma$ -phase of permalloy.

Let us construct the temperature dependence of the normalized asymmetry of scattering in logarithmical coordinates (Fig. 7). We take into account that the Curie points are different for the  $\alpha$ - and  $\gamma$ -phases: they equal  $T_{Cb}^{(\gamma)}$  (FeNi<sub>3</sub>) and  $T_{Cb}^{(\alpha)}$  (Fe) for austenite and martensite, respectively. This allows us to determine the values of critical indices for the surface magnetization of these phases according to expression (6). The corresponding values calculated from the slopes of the straight lines

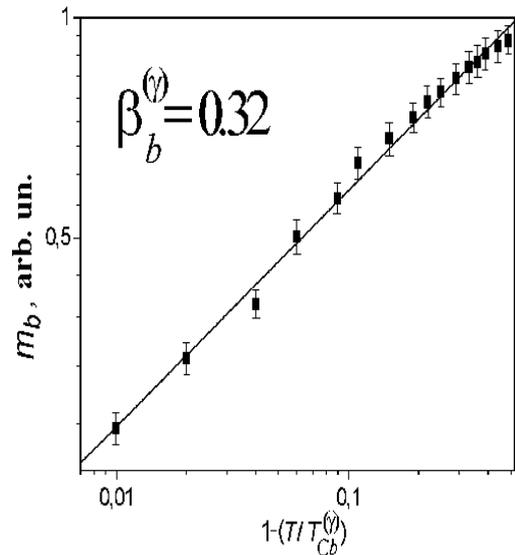


Fig. 8. Logarithmic temperature dependences of the normalized bulk magnetization for the  $\gamma$ -phase of FeNi<sub>3</sub> alloy

are:  $\beta_s^{(\gamma)} = 0.67$  and  $\beta_s^{(\alpha)} = 1.12$ . The critical index for the bulk spontaneous magnetization of FeNi<sub>3</sub> alloy was determined using the data taken from [43] (see Fig. 8). As a result, the value  $\beta_b^{(\gamma)} = 0.32$ , which is twice smaller than that for the surface of the  $\gamma$ -phase, was obtained. This means that the temperature dependence of the spontaneous magnetization for the surface is closer to a linear function in comparison with that for the bulk. The slightly greater values of critical indices for the surface magnetization, namely  $\beta_s^{(\gamma)} = 0.79 \pm 0.02$  and  $\beta_s^{(\gamma)} = 0.769 \pm 0.02$ , were obtained for Ni (100) and (110) in [8] and [20], respectively. Some discrepancies which can be noticed result likely from the presence of a stochastic deviation in the experimental data and from the necessity to choose the temperature interval which is at some distance from the Curie point of bulk FeNi<sub>3</sub> alloy for the analysis. We recall that, at temperatures exceeding  $\sim 650$  K, the segregation of precipitates of the new  $\alpha$ -phase occurs. However, according to the terminology used in [4], the ferromagnetic phase transition occurring in the near-surface region of  $\gamma$ -alloy FeNi<sub>3</sub> and Ni should be considered as the ordinary transition. It is in the case of the ordinary transition that the influence of the surface is negligible: the transition occurs simultaneously in the whole volume of a specimen, and the role of the surface consists only in the fact that the temperature dependence of the surface magnetization differs from the bulk one.

The critical index for the surface magnetization of the  $\alpha$ -phase is  $\beta_s^{(\alpha)} = 1.12$ , i.e. greater than one. However, the ferromagnetic phase transition for the superficial  $\alpha$ -phase is also the ordinary transition most likely. Indeed, the critical index  $\beta_s^{(\alpha)}$  characterizes not only the temperature dependence of the surface magnetization of the  $\alpha$ -phase; it depends also on its amount. This means that upon the heating of the specimen, a decrease in the superficial spontaneous magnetization of the  $\alpha$ -phase occurs not only due to the reduction in the degree of long-range order characteristic of the atomic magnetic moment orientation, but also due to the decomposition of the  $\alpha$ -phase precipitates resulting from the inverse thermoelastic martensitic phase transformation.

## 5. Conclusions

It should be noted that just the investigation of the surface magnetism and the magnetism of thin films by the spectroscopy of spin-polarized electrons gives the unique information which cannot be obtained with the use of other methods. Besides the effects noted above, the advantages of this method include (i) a componentwise investigation of the magnetic properties of materials on the basis of the determination of the spin polarization of Auger electrons [1, 44], (ii) observation of magnetic domains on the surface by scanning electron microscopy with a high space resolution [21,45,46], (iii) effect of adsorption on the superficial magnetic properties [21,47,48]. The analysis of literature data shows that the majority of investigations exploiting the spin-polarized electrons are aimed at studying the magnetic materials now. The advancements in this technique, as well as in the methods of the fabrication of thin magnetic films, will result in the creation of a basis for advanced technologies, in particular, those for the information storage and the development of novel magnetic materials for microelectronics.

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ВЗАЄМОЗВ'ЯЗОК МАГНІТНИХ ВЛАСТИВОСТЕЙ  
З ФАЗОВИМ СКЛАДОМ ПОВЕРХНІ ПЕРМАЛЮЮ  
FeNi<sub>3</sub> ГРАНЬ (111)

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Резюме

Проведено дослідження впливу атомної структури, елементно-го і фазового складу на поверхневі магнітні властивості сплаву FeNi<sub>3</sub>, грань (111). Встановлено, що термостимульоване сегрегаційне збагачення поверхневого шару залізом спричинює передчасне розупорядкування атомів у цьому шарі й протікання мартенситних структурно-фазових ( $\gamma \rightleftharpoons (\alpha + \gamma)$ ) перетворень у ньому. Внаслідок існування тісного взаємозв'язку поверхневої спонтанної намагніченості з фазовим складом спостерігається складний характер температурної залежності спин-обмінної асиметрії розсіяння пучка повільних поляризованих електронів. Так, з ростом температури зразка (починаючи від кімнатної) спин-обмінна асиметрія розсіяння, пов'язана зі спонтанною намагніченістю поверхні, двічі змінює свій знак, а потім зникає при температурі, близькій до точки Кюрі  $\alpha$ -заліза. Показано, що зміни знака спин-обмінної асиметрії розсіяння зумовлені існуванням антиферомагнітного зв'язку між спінами атомів преципітатів  $\alpha$ -фази та  $\gamma$ -фазою пермалюю FeNi<sub>3</sub>. Знайдено, що кількість преципітатів  $\alpha$ -фази, що виділяються у приповерхневому шарі, не монотонно залежить від температури і досягає максимальних значень поблизу точок фазових перетворень порядок-непорядок чи температури Кюрі для об'єму сплаву FeNi<sub>3</sub>.