57Fe and 151Eu Mössbauer studies of 3d-4f spin interplay in EuFe2−xNixA2s

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The EuFe2−xNixA2 (with 0 ≤ x ≤ 0.4) compounds exhibiting 3d and/or 4f magnetic order were investigated by means of 57Fe and 151Eu Mössbauer spectroscopy. Additionally, results for EuNi2As2 are reported for comparison. It was found that spin-density-wave order of the Fe itinerant moments is monotonically suppressed by Ni-substitution. However, the 3d magnetic order survives at the lowest temperature up to at least x = 0.12 and it is certainly completely suppressed for x = 0.20. The Eu localized moments order regardless of the Ni concentration, but undergo a spin reorientation with increasing x from alignment parallel to the a-axis in the parent compound, toward c-axis alignment for x > 0.07. Change of the 4f spins ordering from antiferromagnetic to ferromagnetic takes place simultaneously with a disappearance of the 3d spins order what is the evidence of a strong coupling between magnetism of Eu2+ ions and the conduction electrons of [Fe2−xNixA2]2− layers. The Fe nuclei experience the transferred hyperfine magnetic field due to the Eu2+ ordering for Ni-substituted samples with x > 0.04, while the transferred field is undetectable in EuFe2As2 and for compound with a low Ni-substitution level. It seems that the 4f ferromagnetic component arising from a tilt of the Eu2+ moments to the crystallographic c-axis leads to the transferred magnetic field at the Fe atoms. Superconductivity is not observed down to 1.8 K, although a comparison with 57Fe and 151Eu Mössbauer data for EuFe2As2-based superconductors indicates a similar magnetic structure.

The EuFe2As2-based compounds are unique laboratory for investigations of interplay between magnetism and superconductivity (SC), as well as they are a playground for peculiar competition between itinerant 3d magnetic order of the spin-density-wave (SDW) type and the localized 4f magnetic moments. EuFe2As2 belongs to the “122” family of parent compounds of iron-based superconductors, the same as AFe2As2 (A = Ca, Sr, Ba)1. It crystallizes in the tetragonal ThCr2Si2-type structure with a space group I4/mmm at room temperature, distorted into orthorhombic structure with space group Pmmm upon cooling. Structural transition is accompanied by the Fe-3d itinerant SDW ordering at TSDW = 190 K with saturation moment Msat = 0.99 µB along a-axis. The Eu-4f localized magnetic moments order in an antiferromagnetic (AFM) A-type structure at TN = 19 K with effective moment µeff = 7.94 µB. The neutron diffraction studies suggest rather weak coupling between the Fe and Eu magnetism, but it was found that the strength of interplay between 3d and 4f electrons can be tunable by chemical doping. The Fe magnetic order drives the structural phase transition, which indicates a strong coupling between structural and magnetic components. The Eu2+ ions are located in the planes perpendicular to the c-axis separating [Fe2As2]2− layers. They are in a divalent S7/2 state without orbital contribution to the 4f magnetic moments and a spin-only moments are aligned along the crystallographic a-axis. The A-type order of Eu2+ moments means that they are coupled ferromagnetically within the plane and antiferromagnetically between the planes. Adjacent europium planes are about 6 Å apart, hence direct overlap of interplanar 4f orbitals can be neglected. It can be assumed that the charge carrier mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is responsible for the AFM exchange between interplanar Eu moments. An interesting observation is a field-induced spin reorientation in the presence of a magnetic field along both the a and c axes, which causes that the ground-state

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AFM configuration of Eu²⁺ moments transforms into a ferromagnetic (FM) structure with moments along the applied field direction. Another interesting effect for EuFe₂As₂ is that the SDW transition is suppressed by applied pressure and bulk superconductivity appears in the pressure range from 2.5 to 3 GPa[4]. The Eu²⁺ AFM order and the Néel temperature Tₙₑël reveal no changes up to 3 GPa, then the applied pressure above 6 GPa causes a 4f spin reorientation and the Eu⁴⁺ FM order, while further pressure increase above 8 GPa results in suppression of the FM state, which is connected with the Eu valence change from a divalent state to a nearly trivalent state.

Superconductivity in EuFe₂As₂-based compounds can be achieved by substitutions on either one of three lattice sites as well as by pressure. There are many possibilities for hole and electron doping or isovalent substitution leading to SC, e.g. Euₓ₋₅Feₓ₋₅As₂ with A = K, Na, La, and EuFe₂₋₅T₁₋₅As₂ with T = Co, Ru, Ir, or EuFe₂₋₅(P₁₋₅)₁₋₅. It is interesting to note, that 4f magnetic order occurs within superconducting material as well, and doping leading to superconductivity usually causes some 4f magnetic moment reorientation (canting) with a generation of the 4f FM component[8–10]. The iron-based superconductors are known as materials for which the SC occurs in proximity to a magnetic instability and the magnetic fluctuations could play a key role in the Cooper pairs formation. Hence, it is important to establish the nature of magnetism in these materials.

The electron doping is achieved by partial substitution of the Fe by Ni in EuFe₂₋₅NiₓAs₂ system with structural stability up to x = 0.4, while the Eu sublattice remains chemically intact. Although Ni-substitution causes suppression of the SDW, nevertheless the SC has not been observed down to 2 K[17].

The Mössbauer spectroscopy for ⁵⁷Fe and ¹⁵¹Eu isotopes is a useful local probe for simultaneous investigations of the mutual interaction between the magnetic Fe and Eu sublattices. It has also been shown that the Mössbauer hyperfine parameters are sensitive to change of the electronic charge modulations in the iron-based superconductors[11–14]. A previous ⁵⁷Fe and ¹⁵¹Eu Mössbauer investigations have found a significant coupling between the 3d and 4f magnetic subsystems in the EuFe₂As₂-based compounds[15–19]. The transferred magnetic hyperfine field from the 3d-Eu order to the Fe nucleus was found in the superconducting state at T = 25 K for the first time by Nowik and Felner for EuFe₂₋₅(P₁₋₅)₁₋₅. An enhancement of Fe spin dynamics closely above superconducting critical temperature and related to enhanced Eu spin fluctuations was reported for superconducting EuFe₂₋₅(P₁₋₅)₁₋₅ and EuFe₂₋₅(T₁₋₅)₁₋₅ with the same substitution level x = 0.2 for T = Co (superconductor) and T = Ni (non-superconductor) show practically the same Mössbauer spectra, confirming that only the Fe magnetic state affects the ordered Eu sublattice direction[17] and the 4f/electronic system is unaffected by the SC transition. Substitution of Eu by K atoms gives rise to superconductivity, but long-range 4f magnetic order is suppressed due to the magnetic moment dilution at the rare-earth site in Euₓ₋₅Fe₂₋₅As₂ system[18]. In Eu(Fe₀.₈₆Ir₀.₁₄)₂As₂, the SDW order is fully suppressed and the Eu⁴⁺ moments order magnetically with an appreciable FM component, which causes resistivity reentrance below the superconducting transition temperature[19]. These brief examples of Mössbauer spectroscopy studies show peculiar phenomena existing in the EuFe₂As₂-based systems due to the 3d-4f spin interplay.

On the other hand, the electron doping by the Ni atoms substituting the Fe atoms causes interesting effects in the iron-pnictide superconducting compounds. In (Euₓ₋₅Feₓ₋₅)₂₋₅NiₓAs₂, the compensation of holes (K doping at the Eu site) by the electrons (Ni doping at the Fe site) leads to the reappearance of the resistivity anomaly presumably due to the SDW transition[20], which is fully suppressed for (Euₓ₋₅Kₓ₋₅)Fe₂₋₅As₂. In particular, the anomaly associated with the SDW is observed at about 200 K for x = 0.24, which is close to the SDW transition temperature for parent EuFe₂As₂. It means that the electron doping almost compensates holes in (Euₓ₋₅Kₓ₋₅)Fe₂₋₅As₂[21]. The itinerant FM ordering associated with the Co/Ni spins was discovered in Eu(0.57Ni)₀.₄₋₅As₂[22], while it is known that the Co atoms do not participate in the magnetic ordering in EuCo₁₋₅As₂[23], where the magnetic order is suppressed due to the magnetic moment dilution at the rare-earth site in EuCo₁₋₅As₂ system[24]. In Eu(Fe₀.₈₆Ir₀.₁₄)₂₋₅As₂ the SDW order is fully suppressed and the Eu⁴⁺ moments order magnetically with an appreciable FM component, which causes resistivity reentrance below the superconducting transition temperature[25]. These brief examples of Mössbauer spectroscopy studies show peculiar phenomena existing in the EuFe₂As₂-based systems due to the 3d-4f spin interplay.

The Ni doping leads to superconductivity of the “112” compound EuFe₂As₂, i.e. the magnetism of the 4f-Eu order at 44 K and the 3d-Fe order at 57 K coexist with the superconducting transition at 14 K for EuFe₂₋₅Niₓ₋₅As₂[26,27]. The Ni doping of the “122” iron-pnictide parent compounds AFe₂As₂ (A = Ca, Sr, Ba) changes these systems in the same following way: 1) the SDW is suppressed with increasing Ni concentration, 2) the SC appears. The maximum critical temperature and optimal substitution level x for AFe₂₋₅NiₓAs₂ (A = Ca[28], Sr[28,29], Ba[30]) are as follows: 15 K for x = 0.06, 10 K for x = 0.18, and 21 K for x = 0.10, respectively. The same effect of the SDW suppression is observed in the fourth member of “122” family, i.e. EuFe₂₋₅NiₓAs₂. Hence, it raised the question “why is it not a superconductor?”. Of course the suspect culprit is the 4f magnetism.

The EuFe₂₋₅NiₓAs₂ system was studied by means of Mössbauer spectroscopy in early years of a fascination with the iron-based superconductors and the results for one composition with x = 0.20 and for selected temperatures were reported[22,28]. The present contribution reports Mössbauer results obtained by means of ⁵⁷Fe and ¹⁵¹Eu spectroscopy applied to systematic investigations of the magnetic properties of the Ni-substituted EuFe₂As₂ compounds with an emphasis on study of the 3d-4f spin interaction.

**Experiment**

Single crystals of EuFe₂₋₅NiₓAs₂ were grown using the Sn flux method. The starting materials, high-purity elements of Ca, Fe, Ni, As, and Sn, were taken in the atomic ratio of Eu:Fe:Ni:As:Sn = 1:1:1:2:5[31]. The constituents elements were loaded into alumina crucibles and placed in silica ampoules sealed under vacuum. The ampoules were heated to 1050 °C and kept at this temperature for 10 h to ensure complete dissolving of all components in molten Sn. Next, the ampoules were slowly (2–3 °C/h) cooled down to 600 °C, then the liquid Sn flux was removed by centrifugation. The crystal lattice constants and phase purity were characterized by powder x-ray
diffraction (XRD) using PANalytical X’Pert Pro diffractometer. Resistivity measurements were performed by the four-probe technique using Quantum Design PPMS system.

$^{57}$Fe Mössbauer spectroscopy measurements were performed in transmission mode for 14.41-keV transition. The samples with $x = 0, 0.04, 0.07, 0.10, 0.12,$ and $0.40$ were selected for this investigation. The RENON MsAa-4 spectrometer operated in the round-corner triangular mode and equipped with the LND Kr-filled proportional detector was applied. The He–Ne laser based interferometer was used to calibrate a velocity scale. A single line commercial $^{57}$Co(Rh) source made by RITVERC GmbH was kept at room temperature. The source linewidth $\Gamma_s = 0.106(5)$ mm/s and the effective source recoilless fraction were derived from fit of the Mössbauer spectrum of 10-μm-thick α-Fe foil. The absorbers were prepared using 31 mg of the EuFe$_{2−x}$Ni$_x$As$_2$ samples in the powder form and mixed with a fine powder of B$_4$C carrier. The absorber thickness (surface density) for $^{57}$Fe Mössbauer measurements amounted to 15 mg/cm$^2$ of investigated material. The SVT-400 cryostat by Janis Research Inc. was used to maintain temperature of absorbers.

$^{151}$Eu Mössbauer transmission spectra for 21.6-keV resonant transition were collected applying $^{151}$SmF$_3$ source kept at room temperature and a scintillation detector. The samples with $x = 0, 0.07, 0.10, 0.12,$ and $0.40$ were selected for this investigation. Additionally, the sample of EuNi$_2$As$_2$ was measured. The absorbers were made in the same way, albeit they contained about twice as much the EuFe$_{2−x}$Ni$_x$As$_2$ material per unit area. Data for $^{57}$Fe and $^{151}$Eu Mössbauer hyperfine parameters were processed by means of the Mosgraf-2009 software within the transmission integral approximation. Europium and iron nuclei in EuFe$_{2−x}$Ni$_x$As$_2$ experience almost axially symmetric electric field gradient (EFG) with the principal component aligned with the c-axis of the crystallographic unit cell. The $^{57}$Fe spectra with SDW component were processed by treating the electric quadrupole interaction in the first order approximation. Remaining spectra were processed by application the full Hamiltonian diagonalization in both nuclear states. The europium hyperfine anomaly (the Bohr-Weisskopf effect) was accounted for $^{151}$Eu spectra. The spectral center shifts are reported with respect to the center shift of the room temperature α-Fe or room temperature $^{151}$SmF$_3$ source, respectively.

Mössbauer spectra evaluation within SDW model. A transmission integral approximation has been applied to fit Mössbauer spectra exhibiting magnetic hyperfine interaction. The SDW magnetism should be viewed as modulations of the spin polarization of the itinerant electrons. The absorption profile of the SDW magnetism for such high nickel concentration. The europium magnetic ordering is seen as much less pronounced as $x = 0.20$ and $x = 0.40$ due to lack of this type of resistivity anomaly associated with SDW order is invisible for $x = 0.20$ and $x = 0.40$ due to lack of this type of magnetic interaction. On the other hand, the spin scattering is reduced owing to the increasing spin order. The first mechanism leads to a sharp uplift of resistivity at low temperatures, while the second to the downturn of the resistivity with lowering of the temperature. The resistivity anomaly associated with SDW order is visible for $x = 0.20$ and $x = 0.40$ due to lack of this type of magnetism for such high nickel concentration. The europium magnetic ordering is seen as much less pronounced kink on the resistivity at about 20 K. The SC is not observed down to 1.8 K for any of these compounds.

Results and discussion

Lattice parameters and electrical resistivity. Lattice parameters of the tetragonal unit cell of EuFe$_{2−x}$Ni$_x$As$_2$ at room temperature are shown in Fig. 1. In the range from $x = 0$ to $x = 0.40$, the lattice constant $a$ increases slightly by about 0.3%, while the constant $c$ contract by 1.1%. Hence, the volume of the unit cell decreases by 0.5%, leading to the more compact packing of the [Fe$_x$As$_y$] layers and a decrease in the distance between Eu planes.

Figure 2 shows relative resistivity plotted versus temperature for various nickel concentrations $x$. A sharp uplift of resistivity is visible for $x = 0$ and $0.04$ at about 190 K and 165 K, respectively, while a broad hump appears for $x = 0.07, 0.10$ and 0.12 starting at about 130 K, 90 K and 65 K respectively. Both behaviors are caused by the iron magnetism, but with a gradual ordering of 3d spins in the second case. Upon entering the magnetic state, the metallic behavior changes due to partial gapping of the Fermi surface leading to decrease of the carrier concentration. On the other hand, the spin scattering is reduced owing to the increasing spin order. The first mechanism leads to the upturn, while the second to the downturn of the resistivity with lowering of the temperature. The resistivity anomaly associated with SDW order is invisible for $x = 0.20$ and $x = 0.40$ due to lack of this type of magnetism for such high nickel concentration. The europium magnetic ordering is seen as much less pronounced kink on the resistivity at about 20 K. The SC is not observed down to 1.8 K for any of these compounds.

$^{57}$Fe Mössbauer measurements. Magnetic hyperfine interactions. $^{57}$Fe Mössbauer spectra measured at selected temperatures of 4.2, 25, 80 and 300 K are shown in Fig. 3. The 25 K was chosen because it was the lowest...
temperature of our measurements without europium magnetic order. Spectra were fitted with the SDW model in the magnetically ordered region and with a quadrupole doublet otherwise. Apart from the spectra for the parent compound and the spectra for the compound with the highest Ni content, all other spectra were fitted with superposition of two components. Spectra at 300 K have a shape of pseudo-single line due to small electric quadrupole hyperfine interaction. The precise case is that they are unresolved spectral doublets with small average quadrupole splitting ranging from about 0.1 mm/s for the parent compound to about 0.2 mm/s for the compound with the highest substitution level x = 0.40. An asymmetrical spectral broadening is observed with increasing x due to doping-induced disorder and perturbation of the Fe plane site by the Ni atoms. Spectra at 25 K and 80 K have a shape resulting from the coexistence of the magnetic component and the "non-magnetic" second component. The magnetic spectral component associated with SDW order is described by the average magnetic hyperfine field $<B>$. The second spectral component is described by the average quadrupole splitting $<\Delta>$ and has significantly broadened line-width. The latter component at the low temperatures was fitted applying some hyperfine magnetic field $B_Q$ with a low value of about 1 – 2 T. Further broadening of spectra and change of their shape are observed at 4.2 K and it results from the hyperfine transferred field $B_t$ from ordered magnetic moments of the Eu$^{2+}$ atoms. The presence of two spectral components is somewhat similar to the so-called double-Q magnetic phase with spatially non-uniform magnetization caused by a coherent superposition of two SDWs, leading to both constructive and destructive interference of the SDWs on alternate Fe sites$^{35}$. The spin amplitudes at the Fe sites are nonuniform, vanishing on half of the sites and doubling on the others. But this scenario requires a constant ratio between contribution of both spectral components, which, as will be shown further in the article, is not the case of EuFe$_{2-x}$Ni$_x$As$_2$ system.

Spectra of EuFe$_{1.96}$Ni$_{0.04}$As$_2$ compound across magnetic transition are shown in Fig. 4. The magnetic component with low hyperfine field of 1.5 T appears at 200 K. Its contribution and the magnetic field increase with decreasing temperature. Half of the iron moments are magnetically ordered at about 175 K and the complete order of all iron spins is observed at 4.2 K with $<B> = 7.1$ T, which is comparable to $<B> = 8.1$ T for the parent compound. The transferred hyperfine field at iron due to the magnetic ordering of europium is undetectable for

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**Figure 1.** Lattice parameters of the tetragonal unit cell (space group $I4/mmm$) at room temperature for obtained EuFe$_{2-x}$Ni$_x$As$_2$ samples.

**Figure 2.** Temperature dependencies of the relative resistivity (normalized to the resistivity at 300 K) for EuFe$_{2-x}$Ni$_x$As$_2$ samples. The current was applied perpendicular to the c-axis. The resistivity anomaly associated with the iron magnetism is clearly visible for all studied samples, except the highest Ni-substitution levels $x = 0.20$ and 0.40.
EuFe$_{2-x}$Ni$_x$As$_2$ with $x=0$ and 0.04. Since the Fe plane is in the middle of the distance along the $c$-axis between adjacent Eu planes, hence, in the case of $\theta=90^{\circ}$, the $B_t$ is zero due to a cancellation of the internal magnetic induction from the nearest-neighbor Eu planes of FM-aligned moments corresponding to an A-type collinear AFM state. However, it should be mentioned that some small increase of the Fe hyperfine field of about 0.2 T around temperature of the Eu order in the parent compound EuFe$_2$As$_2$ was reported by Ikeda et al.\textsuperscript{36}. Processing of our spectra for $x=0.07$, 0.10, and 0.12 at 4.2 K gives the transferred field with fairly similar values for both spectral components and with clearly visible difference in the shape of the spectra compared to the temperature of 25 K, i.e. before the Eu magnetism.

The contribution of SDW magnetic component $A$ together with its average magnetic field $<B>$ versus temperature are shown in Fig. 5. The EuFe$_{2-x}$Ni$_x$As$_2$ compounds with $x=0.07$, 0.10, 0.12 contain a predominant contribution of the SDW phase at the lowest measured temperature reaching of about 90%, 80%, 70% respectively. Moreover, a significant reduction of the hyperfine field of the SDW magnetic component to $<B>$ = 5.5, 4.8, 4.6 T at 4.2 K was observed, respectively. Temperature evolution of the SDW hyperfine field $<B>(T)$ for EuFe$_{1.96}$Ni$_{0.04}$As$_2$ was fitted within the model described in Ref.\textsuperscript{38} and compared with the results for EuFe$_2$As$_2$.\textsuperscript{31} The static critical exponent of 0.130(4) and the coherent SDW order temperature of 184(2) K were obtained. We note that the critical exponent in the substituted system EuFe$_{1.96}$Ni$_{0.04}$As$_2$ is almost the same as that in the parent compound\textsuperscript{31}. The value close to 1/8 indicates that the universality class (1, 2) is retained and it means that the electronic spin system with SDW obeys the Ising model (one-dimensional spin space) and has two dimensions in the configuration space (magnetized planes). It is difficult to draw such conclusions for compounds with $x=0.07$, 0.10, 0.12, but one can see that the magnetic ordering starts at about 160, 130 and 100 K, respectively. These temperatures are significantly higher than a temperatures of the resistivity anomaly associated with iron magnetism which are shown in Fig. 2. This is because the Mössbauer spectroscopy is much more sensitive to the electron spin density and even to an incoherent spin density wavelets typical for a critical region of the SDW. The low panel of Fig. 5 shows temperature dependence of a low hyperfine field $B_Q$ resulting from broadening.

**Figure 3.** The $^{57}$Fe Mössbauer spectra of EuFe$_{2-x}$Ni$_x$As$_2$ measured at 4.2, 25, 80 and 300 K. (Inserted values in blue) The relative contribution of the SDW spectral component $A$, the average magnetic hyperfine field of SDW $<B>$, and the hyperfine transferred magnetic field due to the Eu$^{2+}$ ordering for iron in the SDW state. (Inserted values in green) The hyperfine transferred field due to the Eu$^{2+}$ ordering for iron in the "non-magnetic" state (the second spectral component), and the angle $\theta$ between the principal component of EFG at Fe nuclei (i.e. the crystallographic $c$-axis) and the Eu$^{2+}$ magnetic moment. The spectral center shift $\delta$ and the quadrupole splitting $\Delta$ at 300 K are shown. Errors for all values are of the order of unity for the last digit shown.
of the second spectral component. Due to the small contribution of this component, the origin of such weak magnetism and even its existence is doubtful.

The average hyperfine field of SDW $<B>$ for the EuFe$_2$As$_2$ at 4.2 K is 8.1 T and this value is related to 0.99 $\mu_B$ magnetic moment determined from the neutron-diffraction measurements$^2$. Such small moment results from itinerant character of iron magnetism. The Ni-substitution causes decreasing of the hyperfine field $<B>$ and related magnetic moment can be estimated as $<B> = \alpha \mu_{Fe}$, where $\mu_{Fe}$ is the on-site magnetic moment of iron atom and $\alpha$ denotes the constant, which is specific for a given compound$^{37}$. To convert the hyperfine magnetic field to the iron magnetic moment, we used $\alpha = 8.18$ T/$\mu_B$. The average hyperfine field of SDW at 4.2 K and related 3d itinerant magnetic moment of iron versus Ni-substitution $x$ in EuFe$_{2-x}$Ni$_x$As$_2$ system are shown in Fig. 6. The magnetic moment of SDW is halved for the Ni substitution $x = 0.12$ and it decreases linearly in this dopant concentration range. Taking into account the decreasing contribution of SDW component $A$ with increasing Ni content, the weighted average field and corresponding weighted average magnetic moment was presented by triangles in Fig. 6.

**Transferred magnetic field from Eu to Fe.** The EuFe$_{1.96}$Ni$_{0.04}$As$_2$ displays no magnetic dipole hyperfine interaction in the whole studied temperature range, as the SDW does not develop for such high concentration of nickel.

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**Figure 4.** Selected $^{57}$Fe Mössbauer spectra of EuFe$_{1.96}$Ni$_{0.04}$As$_2$ versus temperature across the SDW order. (Inserted values) The contribution of the SDW spectral component $A$, and the average magnetic hyperfine field of SDW $<B>$.
Figure 5. (a) Temperature dependence of the contribution of the SDW spectral component $A$ for Ni-substituted compounds with $x = 0.04, 0.07, 0.10, 0.12$. (b) The average magnetic hyperfine field of SDW $<B>$ versus temperature. The solid lines for $x = 0$ and 0.04 represent the best-fit to experimental data using the model described in Ref. 31. The dashed line for $x = 0.07$ is for the view clarity only. (c) The low hyperfine field of the second spectral component $B_0$ arising from the broadening of spectral lines.

Figure 6. The average hyperfine field of SDW $<B>$ at 4.2 K and corresponding itinerant magnetic moment versus Ni-substitution level $x$ for EuFe$_{2-x}$Ni$_x$As$_2$ system. Triangles represent the weighted average values of both quantities with taking into account the contribution of SDW phase.
One has sole non-magnetic component with clearly visible influence of the transferred magnetic hyperfine field $B_t = 1.38(2)$ T at 4.2 K from europium order. It gives an opportunity to estimate the angle $\theta$ between the principal component of the effective field gradient (EFG) at the Fe nuclei (i.e. the crystallographic $c$-axis in the present case) and the Eu$^{2+}$ localized magnetic moment. It is assumed that the transferred field points in the same direction as that of the Eu magnetic moment. The angle $\theta = 39(1)^\circ$ is determined reliably for this spectrum and indicates canting of europium moments from $ab$-plane of about $90^\circ - \theta = 51^\circ$. The lack of iron magnetism and almost the same angle $\theta = 36^\circ$ for $B_t = 1.37$ T at 4.2 K was found previously for EuFe$_{1.80}$Ni$_{0.20}$As$_2$ by Nowik and Felner$^{29,30}$. The Eu$^{2+}$ spin reorientation phenomenon will be also discussed later in this article based on data from the $^{155}$Eu Mössbauer spectroscopy.

It seems that the transferred field of about 1 T is typical for the EuFe$_2$As$_2$-based compounds with suppressed SDW magnetism and even in the superconducting state. The transferred magnetic hyperfine field acting in the superconducting layer was observed for the first time in the EuFe$_2$As$_2$ system with $x > 0.210$. The advantage of this discovery was that the coexistence of SC and magnetic field in the Fe–As based layer was observed on the same sample under the same experimental conditions, by the local probe, i.e. $^{57}$Fe Mössbauer spectroscopy. The value of $B_t = 0.93(5)$ T was reported for optimally doped superconductor with $x = 0.3$, while $B_t = 0.85(2)$ T for $x = 0.75$, and $0.97(2)$ T for $x = 1$, i.e. EuFe$_2$P$_2$. For the latter case, the angle $\theta = 15(5)^\circ$ was obtained. Another report shows $B_t = 1.2(1)$ T and $\theta = 40^\circ$ for the optimally doped EuFe$_2$As$_2$ superconductor with $x = 0.28$.$^{32}$ Almost the same values of the $B_t$ for different substitution level x indicate that the electron spin density at the position of the Fe nucleus is the same whether the system is normal or superconducting. Another examples of the Eu to Fe magnetic field transfer and the Eu canting are: Eu(Fe$_{0.77}$Co$_{0.23}$)$_2$As$_2$ with $B_t = 1.27(2)$ T and $\theta = 40(1)^\circ$, or Eu(Fe$_{0.57}$Ru$_{0.43}$)$_2$As$_2$ with $B_t = 0.71(2)$ T.$^{33}$ An interesting results of the $B_t = 0.6$ T were reported for the ferromagnetic superconductors AEuFe$_4$As$_4$ (A = Rb$^{39}$ and Cs$^{40}$) with Eu moments laying in the $ab$-plane.

**Electric hyperfine interactions and relative spectral area.** Temperature dependencies of the spectral center shift $\delta$ and the quadrupole splitting $\Delta$ for both spectral components (if present) are shown in Fig. 7. The SDW phase seems to have lower value of the $\delta$ (i.e. a higher value of the $s$-electron charge density than the non-magnetic phase in cases of compounds and temperature ranges where both components occur. But some effect of a fitting artifact can’t be excluded due to a low content of one of the components in the temperature ranges discussed. Hence, the weighted average value of spectral center shift should be considered as a reliable parameter. Generally, the $\delta$ is almost insensitive to Ni-substitution level x and keeps the value of about 0.41 and 0.54 mm/s at temperature of 300 and 4.2 K, respectively. The same insignificant Ni-concentration dependence of the $\delta$ was found for CaK(Fe$_{1.4}$Ni$_{0.6}$)$_3$As$_2$ superconductors.$^{35}$ It means that Ni-doping does not noticeably affect the $s$-electron charge density at the Fe nuclei. From this Mössbauer spectroscopy point of view, the Ni should be considered as isovalent dopant in the EuFe$_{2-x}$Ni$_x$As$_2$ system. However, other effects leading to such an outcome, such as opposite influence of the lattice volume effect and the $d$-electrons shielding effect, cannot be ruled out. Hence, based on these results, the Ni atoms commonly recognized as electron dopant in the EuFe$_{2-x}$Ni$_x$As$_2$ can’t be called into question. The value of $\delta$ indicates that Fe atoms are in a low-spin Fe(II) electronic configuration.

The temperature evolution of weighted average spectral center shift $<\delta>$, shown in Fig. 7, represents a typical second-order Doppler shift dependence on temperature and it could be treated in terms of the Debye model for the lattice vibrations of iron atoms. The Debye temperatures $\Theta_D$, obtained on the basis of this model are typical for a strongly bound metal–covalent system. It increases with Ni substitution level x from about 400 K for the parent compound to about 500 K for $x = 0.10$. On the other hand, further increasing x to 0.40 causes the return to the almost initial value of $\Theta_D$. It means that the (Fe/Ni)–As bonds become stiffer with increasing Ni content up to $x = 0.10$. The $x = 0.10$ is close to the critical substitution level for the AFM-FM transition. It seems that some magneto-elastic effect accompanied by lattice hardening and jump of $\Theta_D$.

The right panel of Fig. 7 shows the parameter of the electric quadrupole hyperfine interaction, i.e. the quadrupole splitting $\Delta$. At 300 K, the $\Delta$ systematically increases from about 0.12 mm/s for the parent compound to about 0.23 mm/s for the Ni-substitution x$= 0.40$. It means that the EFG at iron site increases with x in EuFe$_{2-x}$Ni$_x$As$_2$ system. This is a symptom of an increase in disorder and perturbation of the Fe atoms surrounding in Fe-plane caused by the Ni atoms. The absolute value of $\Delta$ for the "non-magnetic" phase increases as the temperature decreases. At 4.2 K, the $\Delta$ of the SDW phase keeps almost constant and negative value of about $-0.10$ mm/s. This is a manifestation of a greater strength of the magnetic dipole hyperfine interaction than the electric quadrupole interaction, which masks the EFG perturbation caused by increasing Ni substitution. It should be noted that additional magnetic transferred field form europium order perturbs the Mössbauer spectra at 4.2 K. Accordingly, when the 3$d$ magnetism of SDW is weakened by Ni-substitution $x > 0.04$, the 4$f$ transferred magnetism causes difference of the $\Delta$ between 4.2 and 25 K. For $x = 0.40$, for which the iron 3$d$ magnetism was not observed in whole studied temperature range, the 4$f$ magnetism at 4.2 K causes a positive sign of the $\Delta = +0.224(7)$ mm/s (point not shown in Fig. 7).

The Mössbauer recoilless fraction can be approximated by the relative spectral area (RSA), which is defined as:

$$RSA = \left( \frac{1}{C} \right) \sum_{n=1}^{C} \frac{N_0 - N_n}{N_0},$$

where C denotes the number of data channels for folded spectrum, $N_0$ is the average number of counts per channel far-off resonance, namely the baseline, and $N_n$ stands for the number of counts in the channel $n$. The RSA can be directly evaluated from measured spectra as a quantity independent of any physical model. The temperature evolutions of the relative spectral areas for EuFe$_{1.80}$Ni$_{0.20}$As$_2$ with $x = 0.04$, 0.10, 0.40 are displayed in Fig. 8. Here, the RSAs are calculated for the Mössbauer spectra recorded versus increasing temperature in the non-interrupted
Figure 7. Temperature dependencies of the Mössbauer spectroscopy parameters: the spectral center shift δ relative to the shift of room temperature α-Fe, and the electric quadrupole splitting Δ. Values for the SDW spectral component and the second spectral component are shown in blue and in green, respectively. The weighted average spectral center shift <δ> is marked in red along with the solid lines representing the best-fit to experimental data using the Debye model for <δ>(T). The Debye temperature ΘD and the spectral shift at the ground state δ0 are shown. The symbols δ, Δ4.2 and |Δ| stand for measured values of the spectral shift, the quadrupole splitting, and the absolute value of the quadrupole splitting, at 4.2 K and 300 K, respectively. For x = 0.40, point of Δ4.2 with the positive sign determined in presence of the Eu2+ transferred hyperfine field isn’t shown. Note: for 57Fe the sign of the quadrupole coupling constant cannot be determined without the hyperfine field or applied external magnetic field.
The spins between subsequent ab-planes is preserved for these compounds. However, it must be admitted that by fitting the Mössbauer spectra at 4.2 K for EuFe2As2 and EuFe1.93Ni0.07As2 one obtained a slight canting of the Eu2+ moments out of the ab-plane of 13(3)° and 7(6)°, respectively. The same result of 13(7)° and ~ 10° was indicated for EuFe2As2 studied by means of Mössbauer spectroscopy and magnetic torque measurements, respectively. To our knowledge, the canting of Eu2+ moments out of the ab-plane for EuFe2As2 has not been observed (yet) by the neutron diffraction and resonant x-ray measurements. Hence, a wary notation θ ~ 90° is used in Fig. 10.

On the other hand, for x = 0.10 the angle θ between hyperfine field on Eu2+ and the main component of EFG on the same ion amounts to 31(2)° at 4.2 K. The main component of EFG is oriented along the crystallographic c-axis, while the hyperfine field is aligned with the Eu2+ magnetic moment. Hence, the magnetic moment of europium is tilted by 90° − θ = 59(2)° from the ab-plane, while in the parent compounds is perpendicular to the c-axis. It means that in EuFe1.90Ni0.10As2 magnetic moments of Eu2+ tend to rotate on the c-axis in similarity to the superconducting EuFe2As2-based compounds with some canting leading to the ferromagnetic component of the 4f origin.2,10

Another proof of the AFM to FM transition in EuFe1.90Ni0.10As2 is the hyperfine field magnitude of 27.5 T, hence about 1 Tesla higher than for the parent compound and the compound with a slightly lower substitution level x = 0.07. Increased hyperfine field for Eu2+ spins almost aligned along c-axis was observed for EuFe2As2-based substituted compounds.

Both phenomena, i.e. the spin reorientation and the accompanying increase in the hyperfine field, were previously observed by means of the 151Eu Mössbauer spectroscopy for other substituted EuFe2As2-based compounds.
For Eu(Fe0.75Ru0.25)2As2 superconductor with $T_{c_s} = 23$ K, the Eu$^{2+}$ spins order ferromagnetically below 19.5 K with the hyperfine field $B = 28.8$ T at 5 K tilted away from the c-axis by $20(3)^\circ$. For EuRu2As2 one obtained $B = 30.2$ T and $\theta \sim 0^\circ$. For Eu(Fe0.86Ir0.14)2As2 superconductor with $T_{c_s} = 22.5$ K and double reentrance at lower temperature, the Eu$^{2+}$ moments order magnetically at 18 K with an appreciable FM component and the Eu hyperfine field of 28.5 T at 4.2 K. The EuFe2(As1−xPx)2 system preserves the AFM order for $x \leq 0.2$ with the angle $\theta = 77(7)^\circ$ and the hyperfine field $B = 26.2$ T. While, the canting effect and Eu hyperfine field increase with accompanying the Eu to Fe transferred field (~ 1 T) have been observed for $x > 0.2$, with reported values of $\theta = 12(8)^\circ$ and $B = 28.4$ T for $x = 0.316$, or $\theta = 22(3)^\circ$ and $B = 30.8$ T for x = 1, i.e. EuFe2P2.

It can be additionally noted that the FM order of Eu magnetic moments laying in the ab-plane was detected by $^{151}$Eu Mössbauer measurements for superconducting AEuFe4As4 (A = Rb39 and Cs40) with the europium hyperfine field of 22.5 T and 22.4 T, respectively. In this case, the sheets of Eu atoms are separated by the AFe4As4 unit which rules out the possibility of any strong interaction between the Eu planes. In particular, no magnetic coupling is expected to exist between the Eu atoms along the c-direction. On the other hand, the AFM order was reported for parent EuFeAs2 and superconductor EuFeNi0.03As2 with $B = 29.4$ T and 29.1 T, respectively.

Traces of Eu$^{3+}$ makes about 2.6% contribution to the spectra of EuFe1.90Ni0.10As2 in similarity to the superconducting and/or overdoped EuFe2As2-based compounds studied previously by $^{151}$Eu Mössbauer spectroscopy. The Eu$^{3+}$ component of spectra was usually assigned to an unidentified foreign phase or a result of oxidation. But some change in valence of the Eu$^{2+}$ belonging to the main phase due to local chemical pressure induced by nickel substitution cannot be ruled out. However, in the present case one cannot prove that trivalent europium is in the main phase of the sample.

The magnetic structures resulting from $^{57}$Fe and $^{151}$Eu Mössbauer spectra are shown in lower panel of Fig. 10. For parent compound, the Fe-SDW itinerant moments align along a direction and order antiferromagnetically in both a and c directions, while the Eu localized moments align along a direction and order antiferromagnetically in c direction only. The reduction of the Fe moments follows for $x = 0.07$ without changes of the 3d and 4f spins order directions. The further lowering of 3d moment by almost half for $x = 0.10$ results in the 4f spin reorientation.

$^{151}$Eu Mössbauer spectra for compound with iron fully replaced by nickel, i.e. EuNi2As2, are shown in Fig. 11 and the hyperfine parameters are listed in Table 1. We used exactly the same EuNiAs single crystal sample (from the same batch) that was used in Ref. 47, only powdered for our use. This compound possess a tetragonal structure (space group I4/mmm with $a = 4.1145$ Å and $c = 10.091$ Å) at room temperature, similar to EuFe2As2, but without structural phase transition and magnetic ordering of the 3d transition metal (i.e. Ni). The neutron diffraction measurements of this sample47 found that the Eu$^{2+}$ moments form an incommensurate antiferromagnetic spiral-like structure below the Néel temperature of $T_N = 15$ K. They align ferromagnetically...
in the $ab$-plane and rotate spirally by 165.6° around the $c$-axis from layer to layer\textsuperscript{47}. It must be noted, however, that our $^{151}$Eu Mössbauer investigation indicates some canting of the europium moments out of the $ab$-plane and $\theta = 65(2)°$ was obtained. On the other hand, we note that $^{151}$Eu Mössbauer spectroscopy is not sensitive to the rotation of the Eu$^{2+}$ moments around the $c$-axis in this case due to axially symmetric EFG in EuNi$_2$As$_2$ ($c$-axis is the main axis of the EFG) and, therefore, a spiral-like order of Eu$^{2+}$ moments cannot be seen by this method. The EuNi$_2$As$_2$ was studied by $^{151}$Eu Mössbauer spectroscopy in the past\textsuperscript{48}, but unlike our results, negligible quadrupole interaction and some different value of the hyperfine field was reported\textsuperscript{48}.

**Conclusions**

$^{57}$Fe Mössbauer measurements on EuFe$_{2-x}$Ni$_x$As$_2$ show that Ni doping monotonically suppresses the SDW ground state of itinerant magnetic moments and iron diamagnetism is achieved for $x > 0.12$, i.e. certainly for $x = 0.20$. While, $^{151}$Eu Mössbauer spectra indicate that Eu$^{2+}$ magnetic moments order regardless of the Ni-substitution level. However, for the parent EuFe$_2$As$_2$ and for low Ni-substituted compounds up to about $x \leq 0.07$, the localized 4f spins order perpendicular to the $c$-axis, whereas from about $x \geq 0.10$, the magnetic ordering of europium changes from AFM to FM with the angle of deviation from the $c$-axis of about 30°. It seems that the FM order of Eu$^{2+}$ spins causes the transferred hyperfine magnetic field sensed by $^{57}$Fe nuclei. But, it should be noted that some transferred field was also detected for $^{57}$Fe spectrum at the lowest temperature for $x = 0.07$, hence close to the range border of the europium AFM order. However, due to broad magnetic $^{57}$Fe spectrum for $x = 0.07$ at 4.2 K, the transferred field may be somewhat doubtful for this compound and a hypothesis that mainly FM component of the Eu order is responsible for the transferred field seems reasonable. Another explanation that can possibly be proposed is some shielding effect, i.e. the disclosure of the transferred field only after a significant weakening of the iron SDW magnetism caused by the Ni dopant. Also note that Ni substitution in EuFe$_{2-x}$Ni$_x$As$_2$...
reduces $c$ lattice constant of the unit cell (see Fig. 1) and shortens the distance between the Eu planes, which can strengthens the coupling between them.

Based on these and previous results, it can be concluded that the 4$f$-Eu magnetism in the EuFe$_2$As$_2$-based systems is strongly affected by the magnetic behavior of the Fe-As layer. As long as Fe-plane remains unper turbed, for the parent EuFe$_2$As$_2$ and a low substituted compounds for which the 3$d$-SDW order is present, the Fe magnetic anisotropy pulls the Eu magnetic moment direction to be parallel to the ab-plane. On the other hand, a chemical substitution leads to a continuous suppression of the SDW ordering and for the sufficiently substituted compounds (specific to a particular substituent), when the Fe magnetism is strongly suppressed or

| EuFe$_{2-x}$Ni$_x$As$_2$ | T (K) | $\delta$ (mm/s) | $Y_{zz}$ (10$^{22}$ V/m$^3$) | $\epsilon$ (mm/s) | $B$ (T) | $\theta$ (°) | $\Gamma_a$ (mm/s) | $\chi^2$ |
|------------------------|-------|----------------|-----------------|--------------|------|----------|-------------|--------|
| x = 0                  | 300   | -11.46(1)     | -0.39(2)       | -1.55        | -    | -        | 1.52(4)    |
|                         | 4.2   | -11.40(1)     | -0.49(2)       | +0.96        | 26.59(3)| 90       | 1.38(2)    | 0.44   |
|                         | 4.2$^b$ | -11.40(1) | -0.56(4)       | +0.95        | 26.62(4)| 77(3)   | 1.36(2)    | 0.44   |
| x = 0.07               | 300   | -11.59(1)     | -0.37(2)       | -1.45        | -    | -        | 1.58(4)    |
|                         | 4.2   | -11.79(2)     | -0.20(3)       | +0.41        | 26.74(5)| 90       | 1.72(4)    | 0.68   |
|                         | 4.2$^b$ | -11.80(2) | -0.20(5)       | +0.38        | 26.74(6)| 83(6)   | 1.74(4)    | 0.68   |
| x = 0.10               | 300   | -11.43(1)     | -0.34(1)       | -1.36        | -    | -        | 1.42(4)    |
|                         | 4.2   | -11.43(2)     | -0.35(1)       | -1.40        | 27.37(4)| 0        | 1.53(4)    | 0.53   |
|                         | 4.2$^b$ | -1.44(2) | -0.56(4)       | -1.32        | 27.53(5)| 31(2)   | 1.54(4)    | 0.52   |
| x = 0.20$^{17}$        | 5     | -11.75(2)     | -2.35          | -            | 28.7(2)| -        | 1.58(4)    |

**Table 1.** The $^{151}$Eu Mössbauer spectroscopy parameters for EuFe$_{2-x}$Ni$_x$As$_2$ and EuNi$_2$As$_2$. The values for 4.2 K and 5.4 K with superscript "a" were obtained for spectra fitting with fixed angle $\theta$, while superscript "b" corresponds to fitting with free angle $\theta$. The values of respective parameter $\chi^2$ are shown for comparison of the spectra fitting quality. Symbol $\Gamma_a$ stands for the absorber linewidth within transmission integral approximation, while the source linewidth $\Gamma_s = 0.72$ mm/s was kept constant with a value close to the natural width $\Gamma_0 = 0.655$ mm/s. The meaning of the other symbols is described in the text. Figures 10 and 11 show spectra for 4.2$^a$ K and 5.4$^a$ K, respectively. Previous results from Ref.17 and 48 are shown for comparison. Note that the angle $\theta$ is undefined in case of the $V_{zz}$ or $B$ is equal zero.

**Figure 11.** The $^{151}$Eu Mössbauer spectra of EuNi$_2$As$_2$. The meaning of the symbols is the same as in Fig. 10. Description of the magnetic structure of this sample can be found in Ref.47.
absent, the direction of the Eu moments tend to turn parallel to the c-axis and the FM order is partly or fully achieved. The disappearance of the SDW changes the RKKY interaction and increases interplanar coupling which leads to a FM arrangement of the Eu moments. This rearrangement of the 3d spins as the result of the disappearance of the SDW changes the magnetism proves a strong coupling between the magnetism of Eu\(^{2+}\) ions and the conduction electrons of Fe\(_{x}\)Ni\(_y\)As\(_z\) layers. Additionally, the transferred magnetic hyperfine field with value of about 1 Tesla at 4.2 K from the magnetically ordered Eu sublattice to the Fe atoms is observed for substituted samples, but it is undetected for the parent and a low-substituted samples. This effect may result in competition between magnetism and superconductivity in EuFe\(_{2-x}\)Ni\(_x\)As\(_2\)-based superconductors, because the Zeeman effect, which arises due to the parent compound, strongly disfavors formation of the Cooper pair. However, as shown for many EuFe\(_{2-x}\)Ni\(_x\)As\(_2\)-based compounds, this does not prevent the occurrence of superconductivity\(^{19,39,40}\). Eventually, the reentrant effect in some cases was observed\(^{19,20}\). Another effect is the anisotropic resistivity when the interplay between Eu-ferromagnetism and Fe-superconductivity causes zero resistance and diamagnetism only when the supercurrent flows within ab-planes, but in comparison, the out-of-plane resistivity does not go to zero\(^{38}\).

When trying to answer the question posed in introduction of this article “why is EuFe\(_{2-x}\)Ni\(_x\)As\(_2\) not a superconductor?”, it must be said that the phenomena seen by the Mössbauer spectroscopy and described above for this system are the same as for many other EuFe\(_{2-x}\)Ni\(_x\)As\(_2\)-based superconductors. This indicates a similar magnetic structure regardless of whether the system is normal conducting or superconducting. Hence, the reason for the lack of superconductivity in EuFe\(_{2-x}\)Ni\(_x\)As\(_2\) (at least above 1.8 K) is an open question.

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Author contributions
K.K., J.G., A.D., and A.B.—$^{57}$Fe Mössbauer measurements and data analysis, preparation of manuscript and figures; J.Z. and D.R.—$^{151}$Eu Mössbauer measurements and data analysis; M.B. and Z.B.—samples preparation, XRD and resistivity measurements; A.B.—wrote the manuscript text. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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