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Temperature stability of a new type ferromagnetism in a gapless diluted magnetic semiconductor $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) with extremely low concentration of iron impurities

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A new type of ferromagnetism was been studied in a gapless diluted magnetic semiconductor (DMS) $Hg_{1-x}Fe_xSe$ with an extremely low concentration of impurity iron ($x = 0.009$ at.%), which was previously predicted theoretically. Magnetization measurements at two temperatures ($T_1 = 5$ K, $T_2 = 300$ K) in magnetic fields $H = \pm 50$ kOe were carried out. For impurity contributions at both temperatures, magnetization curves $M_H(H)$ were obtained with parameters that are characteristic of ferromagnets. It was determined that the sample under study with a minimum iron concentration $N_{Fe} = 1.8 \cdot 10^{18}$ cm^{-3} ($x = 0.009$ at.%), in addition to a series of $Hg_{1-x}Fe_xSe$ single crystals previously studied by us ($x = 0.012-0.13$ at.%), is included in the hybrid ization interval, in which magnetism of a special type is observed (without inter-impurity interaction). It has been established that the new mechanism of magnetic ordering in a wide temperature range (5−300 K) is due to hybridization effects and exchange interaction of donor conduction electrons, more effective than indirect exchange interaction in conventional DMS (type GaAs:Mn).

Keywords: spontaneous spin magnetism, diluted magnetic semiconductors (DMS), low-concentration *d*-impurities, spin polarization of conduction electrons, spintronics.

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1. Introduction

Diluted magnetic semiconductors (DMS) are of great interest to researchers because their charge and spin degrees of freedom may be used in a single object, which is important when developing modern spintronic devices. Stringent requirements are used for semiconductor spintronics materials: combination of high mobility of charge carriers and stable ferromagnetism to operating temperatures (above room temperature). These criteria are necessary for generation of spin-polarized current and transfer of charge carriers with the same spin orientation into an active area in a real spintronic device [1–4]. Moreover, only this class of semiconductors may provide compliance of lattice parameters with materials used in modern integrated circuits (Ge-based and Si-based). However, DMS's have two serious disadvantages: low Curie temperature (T_C) and crystal structure imperfection. In the recent decade, electronic properties of DMS have been studied extensively, in particular, impurity magnetism of a model $A^{III}B^{V}$ DMS based on GaAs(Mn) [5–8], $A^{II}B^{VI}$ oxide semiconductors based on ZnO with 3*d*-impurities (Fe, Co, Ni, Mn) [9–12], $A^{II}B^{VI}$ semiconductors based on zero-gap HgSe with 3*d*-impurities (Fe, Co, Ni) [4,13–18], ZnTe(Fe,Cr) [19,20], and IV group semiconductors with 3*d*-impurities — SiGe(Fe, Mn) [21–23]. Some progress in the research of increase in the Curie temperature (T_C) has been achieved during this period. Thus, for GaAs(Mn), in which ferromagnetism is observed due to charge carriers (holes), T_C was increased to 200 K [1,6], and the studies of ZnO with 3*d*-impurities detected ferromagnetism induced by structural defects at a temperature above room temperature [9,24–25]. However, DMS retains a relatively low mobility of charge carriers mainly due to defects introduced during synthesis. It has been found that mobility of holes in GaAs(Mn) was $\mu_p \sim 10^2$ cm^2 V^{-1}s^{-1}. A research area focused on spin magnetism in DMS based on group IV semiconductors, in particular, in Mn-doped SiGe films is actively developed [21]. It was found that thermally treated films become ferromagnetic semiconductors in which T_C reached 280 K at Mn concentration ~ 5 at.%. It was found that hole mobility in annealed samples increased significantly and was equal to $\mu_p \sim 10^3$ cm^{2}V^{-1}s^{-1}. Impurity magnetism is studied in detail in ZnO(Mn), in which magnetic ordering at temperatures near room temperature has been predicted earlier [26].

Studies of the impurity magnetism in ordinary DMS are based on the fact that spin ordering is achieved at high concentrations of *d*-impurities ($x \sim 5-10$ at.%) due to interimpurity interaction. The main magnetic ordering mechanism — indirect exchange interaction through charge carrier polarization, and spin ordering are primarily associated with the presence of the second phases or antisite defects, i. e. magnetism in DMS is generally induced [4]. However,

recent study of physical properties of an electronic system formed by donor atoms of low-concentration 3*d*-impurities has justified theoretically and confirmed experimentally the existence of a special spontaneous spin polarization mechanism that is not associated with the interimpurity interaction. Zero-gap DMS based on $Hg_{1-x}Fe_xSe$ with extremely low concentration of Fe ($x < 1$ at.%) was used as an example to show that hybridization of electronic states of the *d*-shell of the transition element impurity atom with crystal conductivity band states forms a single system of donor electronic states which has spontaneous spin polarization when exposed to strong interelectron interaction [27–30]. Spin polarization in such type of electronic system is provided by the same exchange interaction mechanism as takes place in the transition element atom. Occurrence of such spontaneous spin polarization mechanism was theoretically predicted by V.I. Okulov, E.A. Pamyatnykh and V.P. Silin in [31], and later was found experimentally by us when observing abnormal contributions to the Hall resistance of the bulk HgSe single crystals with 3*d*-impurities (Fe, Co, Ni, V, Cr) with low concentration (< 1 at.%) [32–35]. Spontaneous spin polarization of the electronic system was first supported experimentally in state hybridization conditions of the impurity atom's *d*-shell and crystal conductivity band It was shown that there was a special spontaneous spin polarization mechanism that was not associated with the interimpurity interaction, but was caused by the hybridization effects [4]. Studies of the temperature dependences of the magnetic susceptibility of the bulk HgSe single crystals with the 3*d*-impurities (Fe, Co, Ni) with low concentration (< 1 at.%) showed that the paramagnetic susceptibility contained a contribution that met the spontaneous polarization [15]. Study of the temperature dependences of contributions to the heat capacity and moduli of elasticity of the bulk HgSe single crystals with the 3*d*-impurities (Fe, Co) with low concentration (< 1 at.%) demonstrated patterns showing electron-electron „exchange" interaction (exchange interaction of donor conductivity electrons). The description of the temperature dependences of heat capacity and elastic moduli within the framework of the theory of spontaneous spin polarization [31] made it possible to determine the values of the parameters of electron-electron interaction, indicating the presence of spontaneous spin polarization in the electron system under study [4,36–39].

In the study of magnetic field dependences of the magnetization of bulk HgSe single crystals with 3*d*-impurities (Fe, Co) with extremely low concentration (≤ 0.2 at.%), we experimentally discovered for the first time and studied in detail low-temperature ($T = 5$ K) ferromagnetism of a new type (without interimpurity interaction) [16–18]. For impurity contributions, magnetization curves with parameters characteristic of ferromagnets were obtained. Based on the developed theoretical concepts within the framework of the spontaneous spin polarization model [31], good agreement between theoretical and experimental dependences was obtained. The description of magnetization curves according to the developed theory determined parameters characterizing the spontaneous spin magnetism of the studied electronic systems whose values agree with the parameters determined before through the quantitative description of the temperature dependences of magnetic susceptibility [15] and are indicative of the presence of a new type of impurity ferromagnetism. Recently, in [4], we first experimentally discovered a new type of ferromagnetism at room temperature ($T = 300$ K) in a series of bulk $Hg_{1-x}Fe_xSe$ ($0.012 \leq x \leq 0.13$ at.%) single crystals. For impurity contributions, magnetization curves with parameters typical of ferromagnetic materials were obtained. Optical emission spectroscopy and X-ray diffraction analysis results confirmed that the observed ferromagnetism was intrinsic and was associated with the *d*-electrons of the Fe impurity atoms. The exact value of the upper boundary of the hybridization interval in $Hg_{1-x}Fe_xSe$, in which magnetism of this type is observed, was determined: $x = 0.13$ at.%, which corresponds to the value of the impurity iron concentration $N_{Fe} = 2.6 \cdot 10^{19}$ cm^{-3}. The objective of this work was to study the spontaneous magnetization of $Hg_{1-x}Fe_xSe$ with the minimum Fe impurity concentration ($x = 0.009$ at.%) among the whole series of available single crystals in a wide temperature range ($T = 5-300$ K) in order to support experimentally the temperature stability of the new type ferromagnetism, which, according to the spontaneous spin polarization theory [31], is attributable to the exchange interaction of the donor conductivity electrons, doesn't depend on the concentration of the *d*-impurities and may be maintained at high temperatures up to room temperature. Solution of this problem will help determine accurate limits of the hybridization interval (concentrations of the *d*-impurities), in which the new type ferromagnetism is observed, which will provide future opportunity of creating new semiconductor structures (heteroepitaxial layers and low-dimensional structures) with pre-defined (controlled) electronic properties (high mobility and stable ferromagnetism at high temperatures up to room temperature) which is important for the development of semiconductor spintronics.

2. Objects and methods of research

This study investigated the impurity magnetization of the bulk $Hg_{1-x}Fe_xSe$ single crystal with extremely low concentration of Fe impurities ($x \leq 0.01$ at.%) that was grown by the vertical Bridgman method from high purity components (Hg — 99.9999%, Fe — 99.999%, Se — 99.9999%). This method provides high quality single crystals and solid solutions based on mercury chalcogenides and is widely used due to its relative simplicity and high growth rates. Sufficiently high requirements are imposed to this method depending on future application of the grown structure. In particular, when single crystals based on $Hg_{1-x}Fe_xSe$ are grown, bulk defects such as grains shall be removed. In addition, the number of and distribution of Fe impurities along ingots shall be controlled. Special growth

conditions shall be also provided to avoid segregation of the *d*-impurities from the container and environment. After single crystal growth, annealing is usually required. This step is particularly important for ternary solid solutions because the nature of equilibrium intrinsic defects depends on cooling time, temperature gradients and ambient conditions provided during the growth process. The vertical Bridgman method combines all above mentioned factors for successful synthesis of high quality single crystals. Growth technique of semiconductor $Hg_{1-x}Fe_xSe$ single crystals in a wide concentration range of Fe impurities ($0.005 \leq x \leq 10$) at.% is described in detail in [4].

Mercury selenides grown using this method have *n*-type conductivity with the carrier concentration of $\sim 10^{17}\,\mathrm{cm}^{-3}$. Quality control and composition of single crystals was determined using the X-ray diffraction analysis (type of crystal structure, lattice constant, phase composition) and X-ray diffraction micro analysis (Fe concentration and distribution along the ingot). Mobility values were also used to evaluate the quality of grown single crystals. The higher mobility values are, the more perfect crystals are, other things being equal. For $Hg_{1-x}Fe_xSe$ ($x < 1$ at.%) samples studied in our works, mobility is sufficiently high: $\mu_{(5\,\mathrm{K})} \sim 10^5\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (in the hybridization interval), $\mu_{(300\,\mathrm{K})} \sim 10^3-10^4\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (in the hybridization interval) [30,32]. This fact is indicative of high quality of the studied samples.

$Hg_{1-x}Fe_xSe$ single-crystal ingot fabricated using this method had a shape of an elongated cylinder with dimensions 60 mm (length) and 10 mm (diameter). The single crystal is grown along the [110] crystallographic direction. Mean deviation from the specified growth direction during the synthesis was about 3–5%. X-ray microanalysis has shown that the ingot consisted of 3 parts: lower part — Fe-rich, middle part — with concentration of Fe equal in loading ($N_{\mathrm{Fe}} = 2\cdot 10^{18}\,\mathrm{cm}^{-3}$), and upper part — Fe-poor. A disc 2 mm in thickness was cut from the upper Fe-poor part of the ingot and then separated into several parts for X-ray diffraction analysis, elemental analysis and magnetometry. The sample for magnetic measurements had the shape of a rectangular parallelepiped with dimensions of $1 \times 2 \times 8$ mm. The sample preparation procedure for magnetic measurements included several steps: 1) grinding, 2) polishing with diamond paste, 3) chemical etching in 5% bromine solution in isobutyl alcohol (Br_2 — mass fraction at least 99.6%; butanol — C_4H_9OH); 4) rinsing in isobutyl alcohol. Nitrile gloves were used for grinding and polishing to avoid contact between the sample and skin. ProsKit 1PK-101T insulated magnetic tweezers were used for all manipulations associated with chemical etching and rinsing of the sample.

New type impurity magnetism was studied in the $Hg_{1-x}Fe_xSe$ single crystal with extremely low concentration of Fe ($x \leq 0.01$ at.%) at two temperatures: $T_1 = 5\,\mathrm{K}$ and $T_2 = 300\,\mathrm{K}$. Mean concentration of Fe along the ingot length (by loading) — $N_{\mathrm{Fe}} = 2\cdot 10^{18}\,\mathrm{cm}^{-3}$. For the sample with such Fe impurity concentration, the Fermi level ε_{F} is below the donor energy level of Fe ε_d, i.e. at the lower limit of the hybridization range (resonance level), which shall ensure that the condition for the special type of spontaneous spin polarization (without interimpurity interaction) is met (see Figure 1) [30,31]. Electronic parameters of the studied sample: electron concentration $n_e = 3.4\cdot 10^{18}\,\mathrm{cm}^{-3}$, electron mobility $\mu_{\mathrm{e}} = 3.6\cdot 10^4\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (at $T = 5\,\mathrm{K}$); electron concentration $n_e = 2.6\cdot 10^{18}\,\mathrm{cm}^{-3}$, mobility $\mu_{\mathrm{e}} = 8.7\cdot 10^3\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ (at $T = 300\,\mathrm{K}$) [30,32]. Electron mobility at room temperature for the $Hg_{1-x}Fe_xSe$ ($x \leq 0.01$ at.%) sample studied in this work is 6.2 times higher than in pure Si ($\mu_{\mathrm{e}} = 1.4\cdot 10^3\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$) and 2.2 times higher than in pure Ge ($\mu_{\mathrm{e}} = 3.8\cdot 10^3\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$).

Elemental analysis of the studied $Hg_{1-x}Fe_xSe$ sample was performed by the optical emission spectroscopy using the OPTIMA 8000 DV™ (Perkin Elmer™, USA) spectrometer-monochromator to enable accurate determining of Fe impurity content. Optical circuit of the instrument included a high-numerical-aperture double echelle monochromator applied in the range of 160–900 nm with high resolution (better than 0.007 nm at 200 nm). Plasma was operated by a solid-state free-running generator (at 40 MHz). The sample in the form of pray was placed into plasma using the GemTip™ air angular sprayer. Intensity of the Fe impurity was measured at 239.562 nm with axial light sampling. The spectrometer was operated using WinLab32™ software package. X-ray diffraction examinations of the $Hg_{1-x}Fe_xSe$ single-crystal sample were conducted at $T = 300\,\mathrm{K}$ using the Empyrean (Panalytical™, Netherlands) high resolution diffractometer in filtered copper radiation. The diffractometer includes a high resolution goniometer with a minimum interval of 0.0001° and setting repeatability by angles $q - 2q \pm 0.0001^\circ$. Primary data processing and calculation of parameters were carried out using the HighScore Plus 4.1™ software package.

Magnetic measurements were carried out using the MPMS-XL5 SQUID magnetometer (Quantum Design™, USA). The high-sensitivity magnetometer is designed for magnetic property measurements of low-magnetic substances. Specifications (static mode): magnetic moment measurement range ($300-10^{-8}$) emu, magnetic field strength up to 50 kOe, field homogeneity 0.01%, temperature interval (1.8–400) K, temperature stability ~ 0.5%. Magnetic field dependences of magnetization $m(H)$ were studied at two temperatures $T_1 = 5\,\mathrm{K}$ and $T_2 = 300\,\mathrm{K}$ in magnetic fields $H = \pm 50\,\mathrm{kOe}$. External magnetic field orientation was parallel to the [001] crystallographic direction.

3. Experimental findings and discussion

3.1. Optical emission spectroscopy and X-ray diffraction analysis

Elemental analysis using the optical emission spectroscopy of the bulk $Hg_{1-x}Fe_xSe$ ($x \leq 0.01$ at.%) single crystal determined the content of Fe impurity in

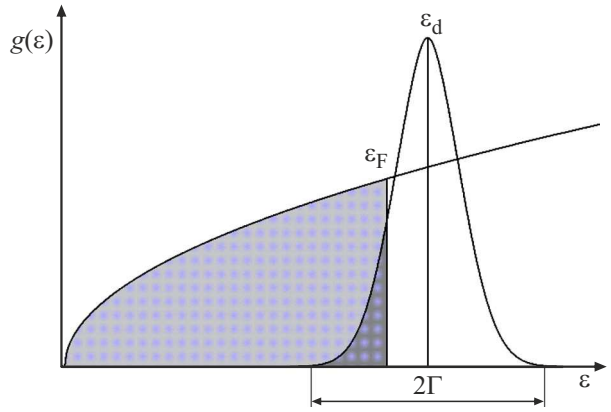

Figure 1. Schematic diagram of the density of electron states $g(\varepsilon)$ and position of the Fermi energy ε_F with respect to the donor level of Fe ε_d in the conductivity band of $Hg_{1-x}Fe_xSe$ ($x \leq 0.01$ at.%) with extremely low concentration of the Fe impurities. Parameters of the impurity level electron structure: $\varepsilon_d = 215$ meV (Fe donor level energy), $2\Gamma = 120$ K (resonance level width) calculated according to the resonance scattering theory when describing the temperature dependences of electron mobility [30].

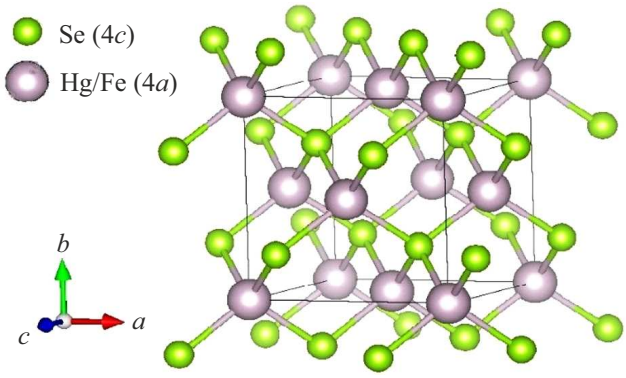

Figure 2. $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) single crystal structure.

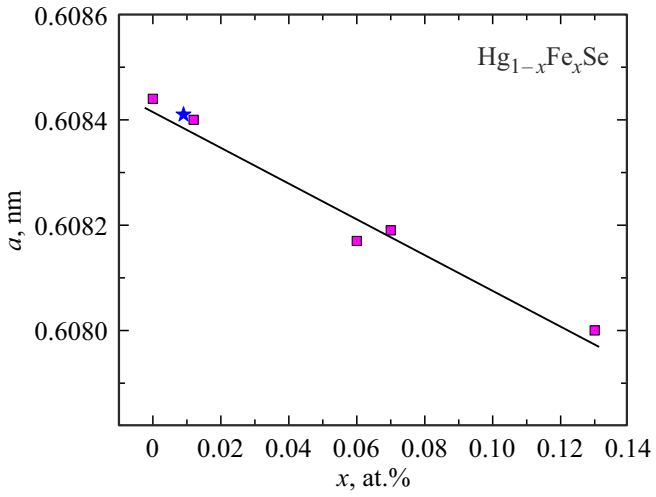

Figure 3. Dependence of the lattice parameter on the Fe impurity concentration: for the $Hg_{1-x}Fe_xSe$ ($0.012 \leq x \leq 0.13$ at.%) single crystals from [4] — marked with boxes, for the $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) single crystal [this work] — lattice parameter is marked with an asterisk.

the studied sample that is close to that with loading ($N_{Fe} = 2 \cdot 10^{18}$ cm^{-3}) and is equal to $N_{Fe} = 1.8 \cdot 10^{18}$ cm^{-3} ($x = 0.009$ at.%). This is the lowest concentration of Fe in the whole series of samples $Hg_{1-x}Fe_xSe$ ($x \leq 0.13$ at.%) on which the impurity magnetization was studied previously [4,17]. Relative error for Fe impurity content measurement in percentage by weight (wt%) didn't exceed 1% in the studied samples. It was also determined that the content of other *d*-elements (Co, Ni, Mn, Cr and V) in the sample was lower than $3 \cdot 10^{17}$ cm^{-3} (< 0.0015 at.%), which meets the known data by the concentration of uncontrolled donors in HgSe [40]. This experimental result confirms that the *d*-electrons of the external shells of Fe impurity atoms are the only source of magnetism in this sample as well as in the series of samples with high concentrations of Fe ($0.012 \leq x \leq 0.13$ at.%) studied by us previously [4], i. e. the studied magnetism is intrinsic and is the property of the $Hg_{1-x}Fe_xSe$ substitutional solid solution.

X-ray diffraction studies showed that the $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) sample was single-phase and had a zinc blende-type cubic structure (sphalerite), space group $F\bar{4}3m$, 216 (Figure 2). In this crystal structure, the Hg atoms are in position (4*a*)and the Se atoms are in position (4*c*). Some positions of Hg (4*a*) are substituted by the Fe atoms. The lattice parameter $a = 0.60841$ nm was determined, the value of which is consistent with the known data for HgSe ($a = 0.6080$ nm) [41]. Crystal lattice parameter measurement error was ± 0.00005 nm max.

Figure 3 shows the dependence of the lattice parameter *a* on the Fe impurity concentration *x* for $Hg_{1-x}Fe_xSe$ ($0.009 \leq x \leq 0.13$ at.%). It was found that the value of the lattice parameter for the 2_1* sample studies herein is well within the linear dependence for the whole series of samples studied by us before [4]. Linear reduction of the lattice parameter from the concentration of the Fe impurities indicates that the $Hg_{1-x}Fe_xSe$ substitutional solid solution is being formed in the structure, i. e. the Fe atoms strictly occupy the Hg atom positions. Thus, the X-ray diffraction analysis results also confirm that the magnetism of the 2_1* sample studied in this work is intrinsic and is attributable to the magnetic moments of the *d*-electrons of the Fe impurity atoms.

3.2. Impurity magnetization

Magnetization was studied on the bulk $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) single crystal — 2_1* sample — with an extremely low concentration of the Fe impurity at two temperatures: $T_1 = 5$ K and $T_2 = 300$ K. Full closed measurement cycle was performed using the SQUID-magnetometer: magnetic field scanning from +50 kOe to −50 kOe and back. Relative error for magnetic moment measurement of sample 2_1* in static mode throughout the magnetic field interval was lower than 2% ($T = 5$ K) and 0.5% ($T = 300$ K).

For the 2_1* sample studied herein, the experimental dependences of magnetization $M_{exp}(H)$ in two

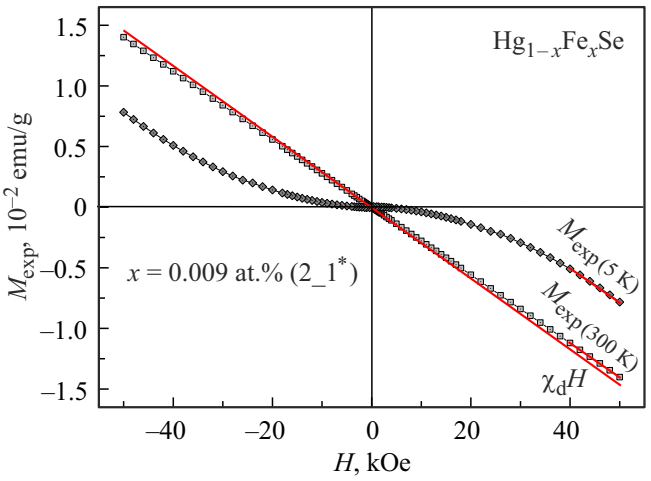

Figure 4. Magnetic field dependences of magnetization $M_{exp}(H)$ of the $Hg_{1-x}Fe_xSe$ single crystal with an extremely low concentration of the Fe impurities ($x = 0.009$ at.%): at $T_1 = 5$ K, $T_2 = 300$ K. $M_{exp(5K)}$ — experimental data at $T = 5$ K, $M_{exp(300K)}$ — experimental data at room temperature ($T = 300$ K), $\chi_d H$ — experimental data for diamagnetic contribution of the HgSe matrix of the studied sample.

magnetic field scanning directions at two temperatures ($T_1 = 5$ K and $T_2 = 300$ K) almost coincided as well as for the series of samples with high Fe concentrations ($0.012 \le x \le 0.13$ at.%) studied in detail before in [4,17]. I.e. a coercive force was not observed. It was determined that the values of this parameter are within the magnetometer error. Figure 4 shows the measurements of the field dependences of specific magnetization $M_{exp}(H)$ of the $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) single crystal at two temperatures ($T_1 = 5$ K, $T_2 = 300$ K) and the experimental data for the intrinsic diamagnetic contribution of the HgSe matrix of the studied $\chi_d H$ sample. Slope of the observed dependence at both temperatures coincides and corresponds to the diamagnetic susceptibility $\chi_d = -2.8 \cdot 10^{-7}$ emu/g · Oe that is close to that of undoped HgSe [41,42].

For studied sample 2_1*, the linear diamagnetic contribution $\chi_d H$ of the HgSe crystal matrix to the full magnetization $M_{exp}(H)$ is significant due to the small concentration of Fe ($x = 0.009$ at.%) that is more than 2 orders of magnitude lower than that in typical DMS ($1 \le x \le 10$ at.%) (Figure 4). It is particularly distinctive at room temperature. Against the background of the diamagnetic contribution to the full magnetization, small deviation from the linear dependence in a low-field measurement range ($H < 20$ kOe) was observed. To determine the ferromagnetic contribution of hybridized impurity states of the Fe atoms, linear dependence on the magnetic field strength, including the matrix diamagnetism, was subtracted from the experimental dependence $M_{exp}(H)$. To plot this dependence $\chi_d H(H)$, linear fitting of the high-field magnetization ($H > 40$ kOe) was performed and the intrinsic diamagnetic contribution χ_d to the full magnetization of the studied sample was determined. Procedure for extraction of the ferromagnetic contribution from the full magnetization of the bulk $Hg_{1-x}Fe_xSe$ ($x < 1$ at.%) single crystals is described in detail in [4]. Using $M_{exp}(H) = M_H + \chi_d H$ (where $M_{exp}(H)$ is the full magnetization of the sample, M_H is the impurity magnetization, $\chi_d H$ is the intrinsic diamagnetic contribution of the HgSe matrix) for studied sample 2_1*, precision procedure for impurity contribution extraction was completed, the dependences $M_H(H)$ were determined and it was found that they attain the saturation as the magnetic field strength grows at both temperature ($T_1 = 5$ K and $T_2 = 300$ K).

Figure 5 shows the impurity contributions $M_H(H)$ to the full magnetization of sample 2_1* at two temperatures. Figures 5, 6 show that both dependences $M_H(H)$ have the form of magnetization curves typical of ferromagnetic materials. However, they differ in the impurity magnetiza-

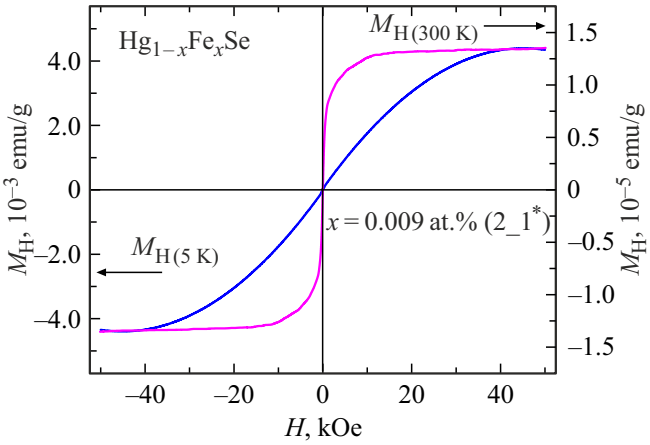

Figure 5. Magnetization of the conductivity donor electron system $M_H(H)$ of the $Hg_{1-x}Fe_xSe$ single crystal with an extremely low concentration of the Fe impurities ($x = 0.009$ at.%): at $T_1 = 5$ K, $T_2 = 300$ K. $M_{H(5K)}$ is the extracted ferromagnetic contribution at $T = 5$ K, $M_{H(300K)}$ is the extracted ferromagnetic contribution at room temperature ($T = 300$ K).

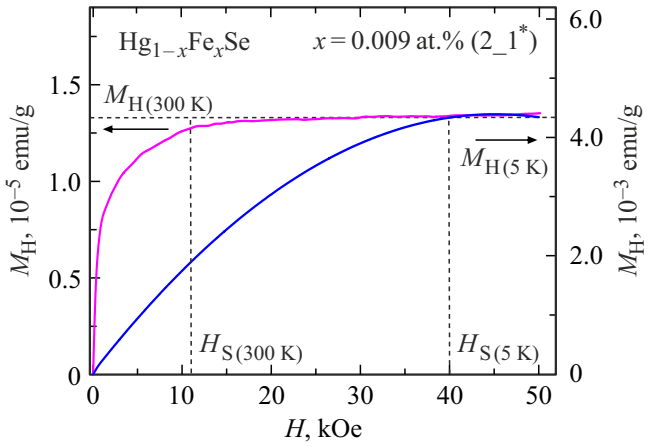

Figure 6. Magnetization curves of the conductivity donor electron system $M_H(H)$ of the $Hg_{1-x}Fe_xSe$ single crystal with an extremely low concentration of the Fe impurities ($x = 0.009$ at.%): at $T_1 = 5$ K, $T_2 = 300$ K.

Table 1. Magnetic parameters of the conductivity donor electrons system in $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%): spontaneous magnetization (M_S), spontaneous magnetic moment per d-electron, (μ_S) and saturation field (H_S) at $T = 5$ K (experimental values of M_S for samples (2_2−6) from [17]). Magnetic parameter values for sample 2_1* — this work

No. Sample	N_{Fe}, 10^{18} cm^{-3} (OES)	x, at.%	M_S, 10^{-2} emu/g		μ_S, $\mu_B/\bar{e}$		H_S, kOe	
			exp.	theor.	exp.	theor.	exp.	theor.
2_1*	1.8	0.009	0.44*	–	**2.0***	–	38.4*	–
2_2	2.4	0.012	0.58	0.6	**1.9**	2.0	39.4	45.0
3	12	0.06	1.8	1.8	**1.2**	1.2	39.9	42.1
4	14	0.07	1.7	1.8	**1.0**	1.1	38.9	44.4
5	26	0.13	1.6	1.7	0.5	0.53	37.9	43.0
6	5.0; 10 (Ga)	0.025; 0.05 (Ga)	0.5	0.5	0.1	0.1	–	–

Table 2. Magnetic parameters of the conductivity donor electrons system in $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%): spontaneous magnetization (M_S), spontaneous magnetic moment per d-electron (μ_S) and saturation field (H_S) (H_S^{AHE} K is the saturation field obtained from the anomalous Hall effect in [32]) at $T = 300$ K (experimental values M_S for samples (2_2−6) from [4]). Magnetic parameter values for sample 2_1* — this work

No. Sample	N_{Fe}, 10^{18} cm^{-3} (OES)	x, at.%	M_S, 10^{-5} emu/g	μ_S, 10^{-3} $\mu_B/\bar{e}$	H_S, kOe	H_S^{AHE}, kOe [32]
2_1*	1.8	0.009	1.3*	**6.1***	11.05*	–
2_2	2.4	0.012	1.7	**5.7**	10.5	10.7
3	12	0.06	3.4	**2.3**	15.6	16.2
4	14	0.07	2.7	**1.6**	13.6	14.0
5	26	0.13	1.0	0.3	12.5	13.2
6	5.0; 10 (Ga)	0.025; 0.05 (Ga)	0.5	0.1	–	–

tion behavior with rising temperature. It was found that the saturation field at room temperature ($T = 300$ K) was equal to $H_S = 11.1$ kOe, which is much lower (almost by 3.5 times) than the saturation field $H_S = 38.4$ kOe at low temperatures ($T = 5$ K).

This result agrees with the experimental data obtained before in our study of the impurity magnetization in the series of bulk $Hg_{1-x}Fe_xSe$ ($x = 0.012-0.13$ at.%) single crystals with higher concentration of Fe impurities [4,17]. This experimental fact indicates that the efficiency of the new type exchange interaction at high temperatures is much higher because spin moment ordering of the d-electrons whose energy levels are in the conductivity band is observed at lower magnetic fields. I.e. the magnetization curves for sample 2_1* at both temperatures have a form similar to that of $M_H(H)$ obtained before in the study of the impurity magnetization of the series of $Hg_{1-x}Fe_xSe$ ($x = 0.012-0.13$ at.%) samples with higher concentration of the Fe impurities [4,17], then the studied sample with an extremely low concentration of the Fe impurity ($x = 0.009$ at.%) is also within the hybridization interval. Moreover, the highest values of μ_S were found exactly for sample 2_1* with the minimum Fe concentration (see Table 1, 2). The hybridization interval previously measured in the experimental and theoretical investigations of the temperature and concentration dependences of kinetic (concentration and mobility of electrons) and thermodynamic (heat capacity, ultrasound, magnetic susceptibility, impurity magnetization) parameters of $Hg_{1-x}Fe_xSe$ ($x < 1$ at.%) included the Fe impurity concentrations $N_{Fe} = (5 \cdot 10^{18}-5 \cdot 10^{19})$ cm^{-3} [4,15,17,30,38].

This study uses the experimental data obtained by means of the optical emission spectroscopy, X-ray diffraction analysis and magnetometry as well as the spontaneous new type magnetization analysis in the bulk $Hg_{1-x}Fe_xSe$ single crystal with the extremely low concentration of the Fe impurity ($x = 0.009$ at.%) to establish new exact limits of the hybridization interval $N_{Fe} = (1.8 \cdot 10^{18}-2.6 \cdot 10^{19})$ cm^{-3}, in which spontaneous spin magnetism of the conductivity donor electrons is observed in a wide temperature range ($T = 5-300$ K).

Table 1 shows the experimental magnetic parameters of the conductivity donor electron system of the $Hg_{1-x}Fe_xSe$ single crystal with the extremely low Fe concentration ($x = 0.009$ at.%) at $T = 5$ K studied in this work, and magnetic parameters (experimental and theoretical) for the

series of $Hg_{1-x}Fe_xSe$ ($x = 0.012-0.13$ at.%) single crystals studied in detail before in [17] for full physical representation. Magnetization curves $M_H(H)$ of the conductivity donor electrons of the $Hg_{1-x}Fe_xSe$ ($x = 0.012-0.13$ at.%) single crystal at $T = 5$ K for the series of samples (2_2–6) were described quantitatively before in [17] according to the spontaneous spin polarization theory developed in [31]. Good agreement of theory and experiment was obtained. Relative measurement error of the saturation magnetization M_S and magnetic moment μ_S when fitting theoretical dependences to the experimental ones was $\sim (5-10)\%$.

Impurity magnetization of Fe-poor sample 2_1* was first studied in this work. Experimental values of the spontaneous magnetization for the series of samples (2_2–6) studied before were taken from [17] at $T = 5$ K and from [4] at $T = 300$ K. Magnetic moments shown in Table 1, 2 were recalculated in this work to consider the Fe concentration measured by the optical emission spectroscopy (OES). This procedure is used to get the content of the d-elements in semiconductor non-magnetic matrices with high accuracy (see Section 2), which allows determination of exact limits of the hybridization interval in which the new type magnetism is observed. In [4,17],values of μ_S were determined taking into account the Fe concentration measured by the X-ray microanalysis (information was provided by process engineers).

It was found that the maximum magnetic moment $\mu_S = 2.0\,\mu_B/\bar{\mathbf{e}}$ at $T = 5$ K was observed for sample 2_1* with the lowest Fe concentration that was studied in this work. I.e. this type of magnetism (without interimpurity interaction) is almost independent on the concentration of the d-impurities and may be observed in DMS at the lowest values ($x < 0.01$ at.%), which agrees with the theory [31]. This experimental fact is also indicative of strong electron-electron interaction of the conductivity donor electrons. The highest values of the spontaneous magnetic moment per the 1d-electron $\mu_S = (2.0-1.0)\mu_B/\bar{\mathbf{e}}$ at $T = 5$ K were determined for the series of samples with Fe concentrations ($x = 0.009$; 0.012; 0.06; 0.07) at.%. Thus, the main magnetic parameters of the studied conductivity donor electron system in $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%) at $T = 5$ K meet the effect of electron-electron interaction, that depends on spin, and are typical of ferromagnetic materials.

Table 2 shows the experimental magnetic parameters of the conductivity donor electron system of the $Hg_{1-x}Fe_xSe$ single crystal with the extremely low concentration of Fe impurity ($x = 0.009$ at.%) at room temperature $T = 300$ K, and magnetic parameters for the series of $Hg_{1-x}Fe_xSe$ ($x = 0.012-0.13$ at.%) single crystals studied before at $T = 300$ K in [4].

It was found that the maximum magnetic moment $\mu_S = 6.1 \cdot 10^{-3}\,\mu_B/\bar{\mathbf{e}}$ at room temperature $T = 300$ K was also observed for sample 2_1* with the lowest Fe concentration that was studied in this work. As long as the maximum magnetic moment is observed at the extremely low concentration of the magnetic impurity ($x = 0.009$ at.%) and at high temperatures ($T = 300$ K), this supports the conclusion on the strong exchange interaction of the conductivity donor electrons in zero-gap $Hg_{1-x}Fe_xSe$, which is more effective than the indirect exchange in ordinary DMS (GaAsMn type). The highest values of the spontaneous magnetic moment $\mu_S = (6.1-1.6) \cdot 10^{-3}\ \mu_B/\mathbf{e}$ at $T = 300$ K were obtained for the same series of samples with Fe concentrations ($x = 0.009$; 0.012; 0.06; 0.07) at.%, as at low temperatures ($T = 5$ K). Thus, the main magnetic parameters of the studied conductivity donor electron system in $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%) at $T = 300$ K also meet the effect of electron-electron interaction and are typical of weak ferromagnetic materials.

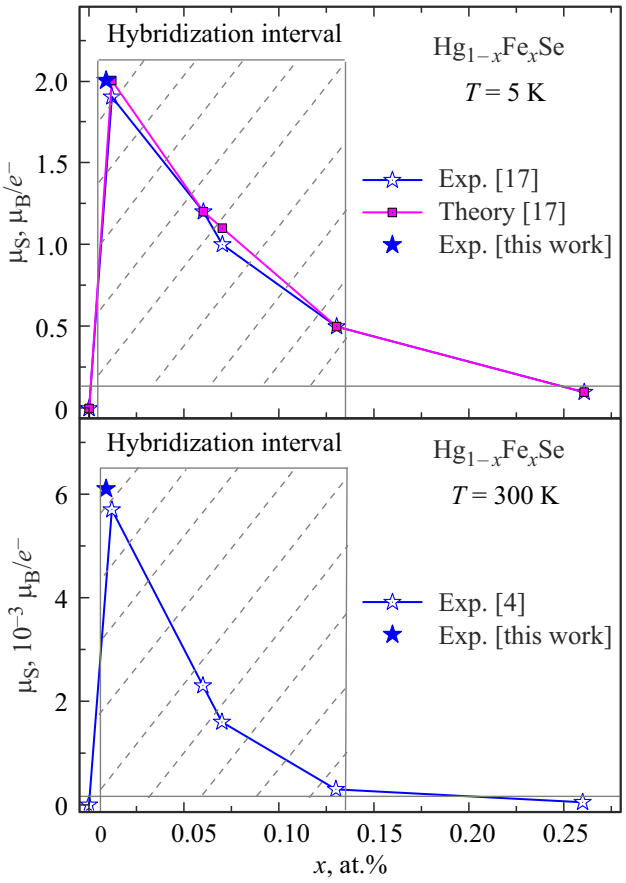

Figure 7. Concentration dependences of the spontaneous magnetic moment μ_S of the conductivity donor electron system of the $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%) single crystal: at $T_1 = 5$ K, $T_2 = 300$ K. Magnetic moments for the series of samples (2_2-6) with Fe concentrations ($x = 0.012-0.13$ at.%) — from our works [4,17]. Asterisk (filled) denotes the magnetic moment for sample 2_1* with the lowest Fe concentration ($x = 0.009$ at.%) studied in this work.

Figure 7 shows the concentration dependences of the spontaneous magnetic moment μ_S of the conductivity donor electron system of the $Hg_{1-x}Fe_xSe$ ($x = 0.009-0.13$ at.%) single crystal at two temperatures: $T_1 = 5$ K, $T_2 = 300$ K.

Figure 7 shows that the concentration dependences $\mu_S(x)$ at both temperatures ($T_1 = 5$ K, $T_2 = 300$ K) have pronounced maxima in the Fe impurity con-

centration region that fall within the hybridization interval ($x = 0.009-0.13$) at.%, which corresponds to $N_{Fe} = (1.8 \cdot 10^{18}-2.6 \cdot 10^{19})\,cm^{-3}$. Results obtained at low temperatures ($T = 5\,K$), agree with the experimental data on the concentration maximum of mobility that was studied before in [30] and is also caused by the electron state hybridization effect of the impurity and crystal conductivity band. It was found that the maximum values of magnetic moment at both temperatures were observed for sample 2_1*, therefore the Fe concentration $N_{Fe} = 1.8 \cdot 10^{18}\,cm^{-3}$ ($x = 0.009$ at.%) is explicitly within the hybridization interval. For sample (5) with $N_{Fe} = 2.6 \cdot 10^{19}\,cm^{-3}$ ($x = 0.13$ at.%), the Fermi energy is at the upper limit of the studied hybridization interval in accordance with the concentration dependences of $\mu_S(x)$ (Figure 7). I.e. samples with Fe impurity concentration within $N_{Fe} = (1.8 \cdot 10^{18}-1.4 \cdot 10^{19})\,cm^{-3}$ are of interest in terms of magnetism, which corresponds to ($x = 0.009-0.07$) at.%, for which the highest values of μ_S were obtained.

Experimental findings of this study of the impurity magnetization of the $Hg_{1-x}Fe_xSe$ single crystal with the extremely low concentration of Fe ($x = 0.009$ at.%) in the wide temperature range ($T = 5-300\,K$) confirm the stability of intrinsic ferromagnetism at extremely low concentrations of the *d*-impurities and at high temperatures up to room temperature. Stability of such type of magnetism in DMS based on $Hg_{1-x}Fe_xSe$ is attributable to the unique electronic (zero-gap) structure, which ensures stability of hybridization effects in a wide temperature range ($5-300\,K$) that lead to the spontaneous spin polarization of the conductivity donor electrons and new type spontaneous magnetism (without interimpurity interaction).

3.3. Spontaneous spin magnetism of conductivity donor electrons

Spontaneous spin polarization of the conductivity donor electrons in the semiconductors with low concentration of the *d*-impurities (< 1 at.%) is described theoretically in [31] on the basis of the quantum Fermi liquid approach. Atomic electron states of the donor impurities of transition elements may be hybridized with the conductivity band states. Electron density of each of these states contains components meeting the combination of partial electron localization on the impurity ion with free motion in the conductivity band. Contribution of the hybridized states of donor electrons of impurity atoms is described by a separate term in density of states of the crystal electron system. Near the resonance impurity level energy ε_r, there is the hybridization interval with the width 2Γ with the density of states $g(\varepsilon)$ that contains terms meeting the free motion $g_c(\varepsilon)$ and localization $n_i\omega_i(\varepsilon)$ of the electron density [17,27]:

$$g(\varepsilon) = g_c(\varepsilon) + n_i\omega_i(\varepsilon), \quad \varepsilon_r - \Gamma < \varepsilon < \varepsilon_r + \Gamma,$$

$$\int d\varepsilon\omega_i(\varepsilon) = 1, \qquad (1)$$

where n_i is the impurity concentration. Hybridization effects are exhibited in physical properties provided that the Fermi energy ε_F is near the donor level ε_d, which is observed for the Fe impurity atoms in zero-gap $Hg_{1-x}Fe_xSe$ ($x < 1$ at.%) (see Section 2, Figure 1). Equation (1) describes the density of electron states of the Fe impurity atoms that introduce one *d*-electron into the hybridization interval [28,30]. Resonance dependence of $\omega_i(\varepsilon)$ and description of the dependence of ε_F on n_i characterizing the population by the state electrons in the hybridization interval are defined in the resonance scattering theory in [27]. States of fife of six *d*-electrons of the Fe impurity atom are in the valence band and have the same polarization, and the state of the remaining *d*-electron meeting the opposite polarization is within the conductivity band and hybridized wit the conductivity band states. Exchange interaction of electrons in hybridized states leads to the occurrence of localized spin density (local magnetic moments) and spin polarization of contribution to electron states that meet the free motion (of conductivity electrons). Localized and distributed electron densities occur due to the resonance scattering effect (hybridization) and meet a single particular energy of each electron. Spin polarization of the conductivity electrons is performed in a more effective way than that in the indirect Rudermann–Kittel exchange.

According to the spontaneous spin polarization theory, part of the energy of hybridized state electrons β associated with the spontaneous spin polarization localized in the state components is a linear function of impurity concentration n_i and thermodynamic mean concentration of conductivity electrons n_e [4,16,31]:

$$\beta = \psi_i n_i + \psi_{ic} n_e, \qquad (2)$$

where ψ_i is the constant of electron-electron interaction of the localized components of hybridized states, ψ_{ic} is the constant of electron-electron interaction of the localized and conducting components of the hybridized states. Equation similar to (2) is also valid for the spontaneous spin polarization to the energy of conducting component of the hybridized electron states. Detection of the spontaneous magnetization exhibited in the conductivity of the donor electron system of the 3*d*-impurities (Fe, Co, Ni, Cr, V) in HgSe:3*d* in the form of anomalous contributions to the Hall resistance was the first evidence of potential existence of such effects at extremely low concentrations of the *d*-impurities (< 1 at.%) [32,33]. Studies of the temperature dependences of the magnetic susceptibility of the hybridized state electron systems of Fe, Co and Ni impurities in HgSe:3*d* showed that the paramagnetic susceptibility contained a contribution that met the spontaneous

polarization [15]. New type low-temperature ($T = 5\,\mathrm{K}$) spontaneous magnetism was studied in detail in [16–18] on the $Hg_{1-x}Fe_xSe$ and $Hg_{1-x}Co_xSe$ ($x < 1$ at.%) systems. The new type ferromagnetism has been recently first found at room temperature ($T = 300\,\mathrm{K}$) on a series of bulk $Hg_{1-x}Fe_xSe$ ($0.012 \le x \le 0.13$ at.%) single crystals for which the Fermi energy is close to the donor-level resonance energy and a condition for hybridization and spin polarization is met. Magnetization curves with parameters that met the effect of electron-electron interaction and were typical of ferromagnetic materials were obtained for impurity contributions. Optical emission spectroscopy and X-ray diffraction analysis confirmed that the observed ferromagnetism was intrinsic and was explicitly associated with the *d*-electrons of the external shells of Fe atoms [4].

This work experimentally studied the spontaneous magnetization of the $Hg_{1-x}Fe_xSe$ ($x = 0.009$ at.%) single crystal with the minimum concentration of the Fe impurity and findings were obtained confirming that the new type ferromagnetism maintained its stability at extremely low concentrations of the *d*-impurities (< 0.01 at.%) and at high temperatures ($T = 300\,\mathrm{K}$), which confirms that the efficiency of the new exchange interaction mechanism of the conductivity donor electrons that was previously predicted theoretically [31].

4. Conclusion

In this paper, by studying the spontaneous magnetization of a bulk DMS single crystal based on $Hg_{1-x}Fe_xSe$ with an extremely low concentration of impurity iron ($x = 0.009$ at.%) in a wide temperature range ($T = 5{-}300\,\mathrm{K}$), we obtained experimental confirmation of the temperature stability of a new type of ferromagnetism in the highly diluted magnetic limit ($x < 0.01$ at.%), which is maintained at room temperature and does not depend on the concentration of *d*-impurities. The observed effect is explained in terms of the developed spontaneous spin polarization theory [31]. A new mechanism of spin polarization of conduction electrons in semiconductors has been established, which operates in a wide temperature range ($5{-}300\,\mathrm{K}$) and is due to the unique (gapless) electronic structure of $Hg_{1-x}Fe_xSe$, hybridization of impurity states and exchange interaction of donor conduction electrons, which is more effective than the indirect Ruderman–Kittel exchange. This mechanism of spin polarization has a certain universality, since it is not associated with interimpurity interactions and therefore can manifest itself at extremely low concentrations of *d*-impurities, as well as in low-dimensional semiconductor structures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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