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Spontaneous spin magnetism of donor conduction electrons of hybridized states of a crystal formed by a system of $3d$-elements impurity atoms of low concentration (< 1 at.%)

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Received September 2, 2021
Revised September 2, 2021
Accepted September 4, 2021

The given work is devoted to the experimental proof of existing the spontaneous spin polarization of the donor electron system of $3d$-transition element impurity atoms of low concentration (< 1 at.%) in a mercury selenide crystal. For this purpose there have been measured the dependences of the magnetization on the magnetic field strength at low temperatures ($T = 5$ K). As a result of the analysis of the obtained dependences, there were extracted the impurity contributions, which are described by the magnetization curves typical of the ferromagnets, and by the magnetic parameters conforming to the spontaneous magnetism of the systems under study, which are unambiguously related to the donor conduction electrons of the outer d-shells of impurity atoms. By its nature, according to the developed theoretical concepts, the spontaneous spin polarization manifests itself in exchange interaction, taking place in hybridizing the electronic states of the impurity atom and the conduction band ones of the crystal.

Keywords: $3d$-impurities of the low concentration, gapless semiconductors, hybridized electronic states, spontaneous spin polarization, low-temperature ferromagnetism

DOI: 10.21883/PSS.2022.01.52488.198

1. Introduction

This paper outlines the results of experimental studies of low-temperature magnetization for a system of donor electrons of impurity iron and cobalt atoms of low concentration (< 1 at.%) in a gapless semiconductor crystal (mercury selenide). The work was aimed at providing an experimental proof of the existing of spontaneous spin-based magnetic ordering of low-concentration electron systems of the $3d$-impurity atoms in a semiconductor crystal.

The final result, presented in full for the first time, pertains to the physics of spontaneous impurity magnetism of semiconductor crystals. The known studies in this field are focused on the implementation of magnetic ordering at a sufficiently high concentration of $3d$-impurities $\sim (3-9)$ at.% and are based on the idea that spontaneous spin polarization of an impurity electron system arises due to inter-impurity interaction that ensures mutual spontaneous polarization of ion cores of impurity atoms [1–3].

In another limit of low concentration for $3d$-impurities (< 1 at.%), ion cores of impurity atoms are heavily rarefied in their location, which hinders the inter-impurity interaction. Therefore, in order to achieve magnetic ordering, attention should be paid to the manifestation of conductivity electrons, which creates (by outermost electron shells of impurity atoms) in the host crystal a donor component of electrons with polarized spins in the conduction band of the. Electron states in an impurity atom and in the conductivity band form unified hybridized donor states that have contemporaneously the properties of free motion, localization, and spin polarization. Exchange interaction between electrons that fill such hybridized states depends on spins and causes spin polarization of their system. Thus, the entire system is a semiconductor crystal with a donor component having low-concentration spontaneous spin polarization.

Justification of the effect of spontaneous spin polarization in a low-concentration system was started in the course of development of the concepts of existence of state hybridization of donor $3d$-electrons in impurity atoms with states of the crystal conductivity band and the associated formation of a spin-polarized system of conductivity electrons. The previously developed theoretical description and the performed experiments were used for a detailed study of the anomalous contribution to Hall resistance of a mercury selenide crystal with low-concentration iron impurities (< 1 at.%). It was shown that the dependence of the anomalous part of Hall resistance on magnetic field strength has the form of a curve with saturation typical for magnetically ordered structures. This result has provided the first proof of the existing of spontaneous magnetization in low-concentration impurity systems [4]. In subsequent studies, regularities, where exchange electron-electron interaction manifests itself, have been found during the study of impurity contributions to moduli of elasticity and heat capacity of the mercury selenide crystal with low-concentration $3d$-impurities (< 1 at.%). It has been showed that the temperature dependence of impurity contribution to heat capacity has a maximum the shape of which depends on intensity of exchange interaction. The dependence observed in the experiments satisfies the presence of spontaneous spin polarization of the electron system under study [5]. The study of temperature dependencies of magnetic susceptibility for electron systems of low-concentration $3d$-impurities in mercury selenide has established that the paramagnetic susceptibility contains a temperature-independent contribution, related to the presence of spontaneous polarization, and has determined the polarization degree of electron density in a localized component of hybridized states for each $3d$-impurity (iron, cobalt, nickel) [6].

Thus, experimental data is available on electron systems of low-concentration $3d$-impurities (< 1 at.%) that have spontaneous spin polarization not related to inter-impurity interaction. Thereat, a specific class of semiconductor objects has emerged and is of interest both for subsequent fundamental research and for possible practical applications. Therefore, there are now two classes among magnetically ordered impurity semiconductor crystals having a low concentration of impurity atoms (< 10 at.%):

1) crystals with a rarefied (diluted) magnetically ordered ion and electronic systems (concentration of d-impurities is $1-10$ at.%);

2) crystals with a non-ordered low-concentration ion system (concentration of d-impurities less than 1 at.%, an order lower than class 1) and a magnetically ordered low-concentration systems of electrons in hybridized states of the conductivity band.

Given below is a description of this work to study only objects of the defined low-concentration class 2 with electrons in hybridized states.

The obtained experimental description of the studied systems as objects having all the typical features of magnetic ordering is given. Since certain concepts of magnetic-field dependencies of magnetization have been established in the spontaneous magnetism physics, a detailed study of magnetic-field dependencies of magnetization, which contain the necessary features of spin ordering, has been accordingly carried out. A group of systems with such concentrations of $3d$-impurities, for which the studied effects of spin polarization are the most considerable, was assigned. Then the following was chosen for experiments: electron systems of iron and cobalt impurities of the limit low concentration (< 1 at.%) in mercury selenide crystals whose thermodynamic and kinetic properties were studied in detail in earlier papers [4–6].

2. Objects and methods of research

The experiments were carried out on two samples with a low concentration of iron and cobalt impurities (< 1 at.%): $N_{Fe} = 7 \cdot 10^{18}\,cm^{-3}$ and $N_{Co} = 2.5 \cdot 10^{18}\,cm^{-3}$. HgSe : $3d$ monocrystals were grown by crystalthe Bridgman method at Chernivtsi National University (group of L.D. Paranchich). Concentration and distribution of d-impurities across the ingot volume were monitored using an X-ray microanalyzer. Sample shape is a rectangular parallelepiped sized $(1 \times 2 \times 8)$ mm. Static magnetic moment was measured by A.F. Gubkin on a SQUID-magnetometer MPMS-5-XL (Quantum Design Co.) at low temperatures $T = 5$ K in magnetic fields of up to 50 kOe (in the FC mode) at Collaborative Access Center „Testing Center of Nanotechnology and Advanced Materials“ of the IMP UB RAS.

3. Experimental results and discussion

Magnetic field dependencies of magnetization $M_{exp}(H)$ of a mercury selenide crystal with a low concentration of iron and cobalt impurities contain linear contributions $\chi_d H$ of diamagnetism of the crystalline matrix (Fig. 1) and impurity contributions $M_0(H)$, that reach saturation as magnetic field intensity grows (Fig. 2).

Diamagnetic contribution was determined according to the asymptotics of the dependence $M_{exp}(H)$ in the region of high magnetic fields $\sim (40-50)$ kOe. The obtained values of diamagnetic susceptibility for both systems (Fe, Co) are close to the known value for an undoped HgSe crystal [7,8]. Magnetization of the impurity electron system $M_0(H)$ is defined by the difference $M_{exp}(H) - \chi_d H$.

The analysis of the obtained experimental dependencies of magnetization $M_0(H)$ (Fig. 2) determines the values of the main magnetic parameters and their comparison with the characteristics related to a system of non-interacting spins. The main parameters include saturation

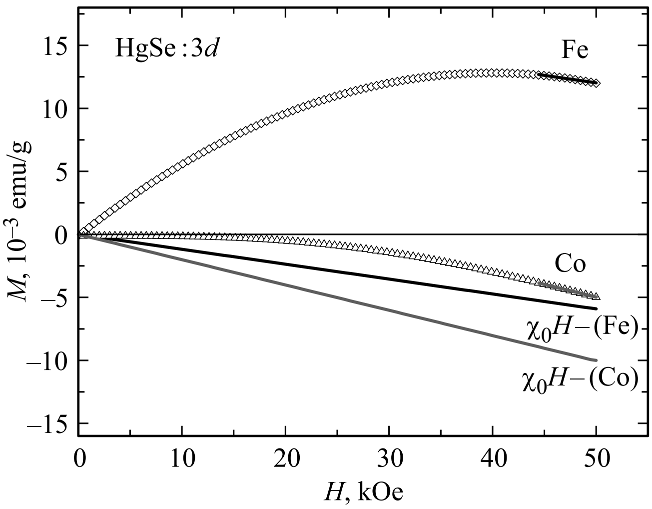

Figure 1. Magnetic field dependencies of specific magnetization $M(H)$ for a HgSe monocrystal with low-concentration $3d$-impurities (< 1 at.%) at $T = 5$ K: $N_{Fe} = 7 \cdot 10^{18}\,cm^{-3}$, $N_{Co} = 2.5 \cdot 10^{18}\,cm^{-3}$ (symbols — experiment, linear dependencies — diamagnetic contributions by the HgSe crystalline matrix to total magnetization).

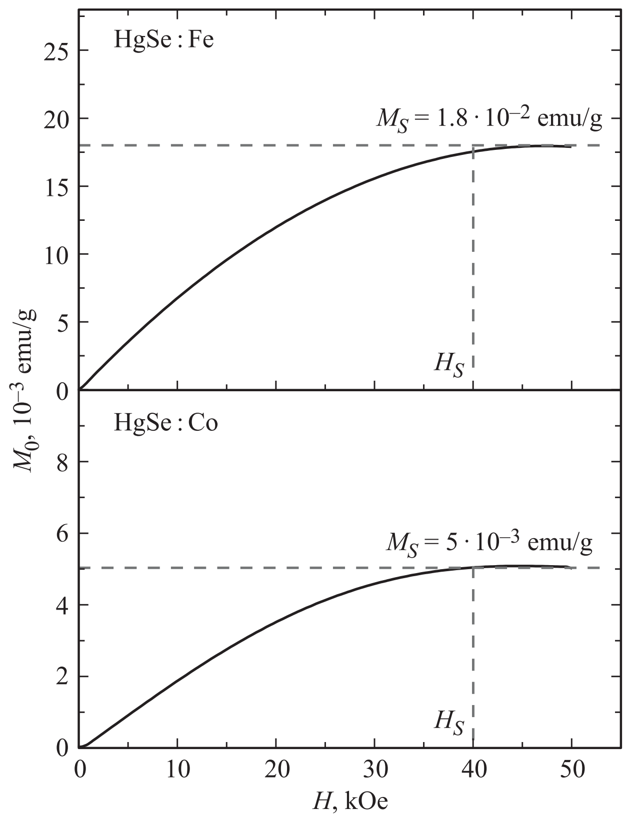

Figure 2. Curves of spontaneous magnetization $M_0(H)$ of a HgSe monocrystal with low-concentration $3d$-impurities (< 1 at.%) at $T = 5$ K: $N_{\mathrm{Fe}} = 7 \cdot 10^{18}\,\mathrm{cm}^{-3}$, $N_{\mathrm{Co}} = 2.5 \cdot 10^{18}\,\mathrm{cm}^{-3}$ (ferromagnetic contribution).

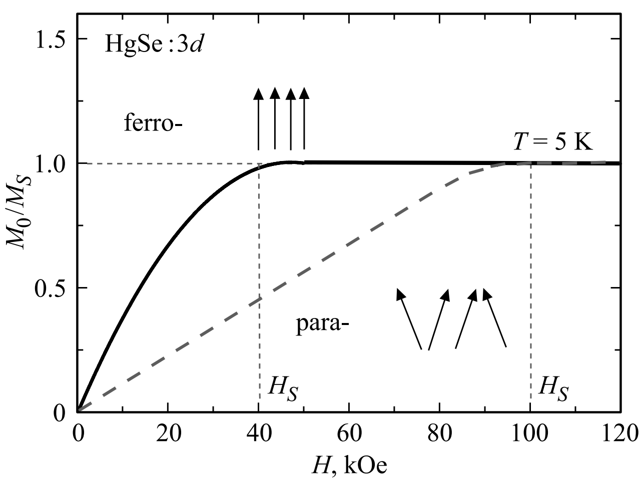

Figure 3. Ratio of spontaneous magnetization M_0 to saturation magnetization M_S for an electronic system of low-concentration $3d$-impurities (Fe, Co) (< 1 at.%) in a HgSe monocrystal (solid line — experiment, dashed line — schematic dependence for the case of non-interacting spin moments).

magnetization M_S and saturation magnetic moment μ_s per one electron. The obtained values of $\mu_s = 2.1\,\mu_B$ and $M_S = 1.8 \cdot 10^{-2}$ emu/g for a system with iron impurities ($N_{\mathrm{Fe}} = 7 \cdot 10^{18}\,\mathrm{cm}^{-3}$) correspond to values that considerably exceed the Bohr magneton, satisfying the saturation of the free electron system. Magnetic parameters for a system with cobalt impurities with the concentration $N_{\mathrm{Co}} = 2.5 \cdot 10^{18}\,\mathrm{cm}^{-3}$: saturation magnetic moment per one electron $\mu_s = 1.5\,\mu_B$ that corresponds to the value $M_S = 5 \cdot 10^{-3}$ emu/g. Another important parameter of the studied magnetization curve $M_0(H)$ is the saturation field (H_s). This experimental value was closed to 40 kOe for both impurity systems (Fe, Co), while for a free electron system the value of H_s at such low temperatures ($T = 5$ K) has a magnitude order of ~ 100 kOe (Fig. 3).

For illustration purposes, Fig. 3 shows the reduced magnetization M_0/M_S at low temperatures ($T = 5$ K): experimental values of spontaneous magnetization M_0 for two impurity systems (Fe, Co) in a HgSe monocrystal were divided by saturation magnetization M_S for iron and cobalt, respectively. The obtained experimental dependencies have coincided and merged into a single magnetization curve, typical for low-concentration magnetically ordered impurity systems. This fact confirms similar nature of spontaneous magnetism related to the manifestation of low-concentration donor impurities or iron and cobalt in a gapless semiconductor crystal, so that electron filling of the conductivity band of the given crystal does not depend on donor impurity type.

Thus, both magnetization curves for the studied impurity systems reflect the ferromagnetic ordering, since they have parameters that satisfy the strong influence of exchange electron-electron interaction that depends on spin.

The obtained results satisfy the direct experimental confirmation of a particular variety of spontaneous spin polarization and magnetic ordering arising in an electron system of $3d$-impurities in the low-concentration limit (< 1 at.%). This fact is not related to inter-impurity influence, but occurs due to the effect of hybridization of impurity electron states in the crystal conductivity band. The presented alternative mechanism of magnetic ordering can act in a wide range of semiconductor objects, including low-dimensional structures.

4. Conclusion

The work results as applied to the set task can be formulated briefly and simply. The work has provided a convincing proof of spontaneous spin magnetic ordering of low-concentration electron systems. However, the need for further development of actions to create new objects and develop physical grounds for the functioning of such systems is equally evident. That's why the results of this work are promising.

Funding

The work has been performed under the state assignment on topic „Electron“ No. AAAA-A18-118020190098-5.

Conflict of interest

The authors declare that they have no conflict of interest.

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