AIP Advances

Curie–Weiss behavior of the low-temperature paramagnetic susceptibility of semiconductors doped and compensated with hydrogen-like impurities

Cite as: AIP Advances **11**, 055016 (2021); https://doi.org/10.1063/5.0048886
Submitted: 27 February 2021 • Accepted: 27 April 2021 • Published Online: 13 May 2021

N. A. Poklonski, A. N. Dzeraviaha, S. A. Vyrko, et al.

COLLECTIONS

This paper was selected as an Editor's Pick

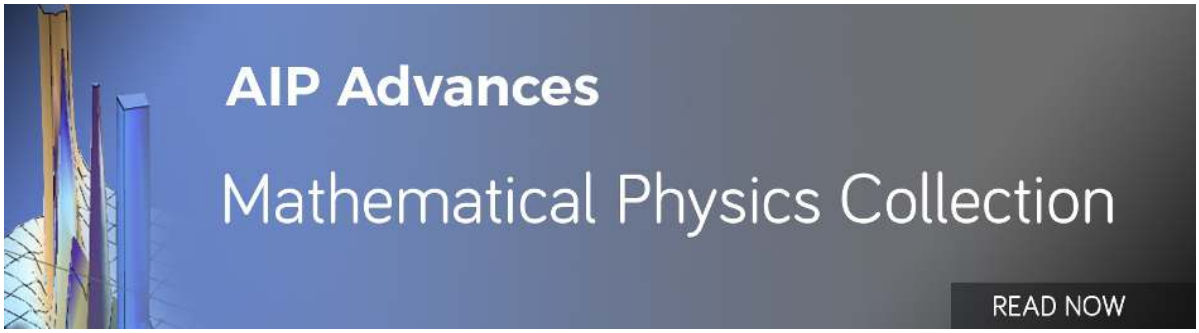
View Online Export Citation CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Tutorial: Basic principles, limits of detection, and pitfalls of highly sensitive SQUID magnetometry for nanomagnetism and spintronics
Journal of Applied Physics **124**, 161101 (2018); https://doi.org/10.1063/1.5045299

Comparison of supercavity geometry and gas leakage behavior between the double-cavity flow pattern and the wake-closure flow pattern
AIP Advances **11**, 055021 (2021); https://doi.org/10.1063/5.0046868

Energy analysis on rebound dynamics of two droplets impacting a superhydrophobic surface simultaneously
AIP Advances **11**, 055007 (2021); https://doi.org/10.1063/5.0046690



© 2021 Author(s).

Curie–Weiss behavior of the low-temperature paramagnetic susceptibility of semiconductors doped and compensated with hydrogen-like impurities

Cite as: AIP Advances 11, 055016 (2021); doi: 10.1063/5.0048886
Submitted: 27 February 2021 • Accepted: 27 April 2021 •
Published Online: 13 May 2021

View Online Export Citation CrossMark

N. A. Poklonski,[1,a)] A. N. Dzeraviaha,[1] S. A. Vyrko,[1] A. G. Zabrodskii,[2] A. I. Veinger,[2] and P. V. Semenikhin[2]

AFFILIATIONS

[1]Physics Department, Belarusian State University, Nezavisimosti Ave. 4, 220030 Minsk, Belarus
[2]Ioffe Institute, Politekhnicheskaya 26, 194021 Saint-Petersburg, Russia

[a)]Author to whom correspondence should be addressed: poklonski@bsu.by

ABSTRACT

For the first time, a quantitative model of the Curie–Weiss behavior of a low-temperature paramagnetic susceptibility of electrically neutral donors in n-type diamagnetic covalent semiconductors is proposed. The exchange interaction between nearest two neutral donors was calculated with the use of the Heitler–London model. In this model, we take into account the change in the thermal ionization energy of donors due to the shift of the bottom of the conduction band to the bandgap with doping and compensation. The energy of the exchange spin–spin interaction between electrons localized on donors is calculated as a function of the donor concentration and the degree of their compensation by acceptors. The broadening of the donor band due to the Coulomb interaction of the nearest impurity ions was taken into account. We considered crystals of n-type germanium doped with arsenic up to the concentration close to the insulator–metal phase transition (Mott transition) and compensated with gallium. The compensation ratio K is the ratio of the concentration of compensating acceptors KN to the concentration of doping donors N. The model predicts a change in the sign of the Curie–Weiss temperature from minus to plus (a transition from the antiferromagnetic to ferromagnetic local ordering of electron spins on donors) for $K \approx 0.15$–0.3, reaching its maximum positive values of ≈ 1.3 K for $K \approx 0.5$ with the following decrease (a transition to paramagnetism) for $K > 0.85$. The calculated behavior of the paramagnetic susceptibility of donors is consistent with the experimental data for compensated n-Ge:As,Ga samples close to the Mott transition.

© 2021 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/5.0048886

I. INTRODUCTION

Despite the more than half a century history of study of the electron spin resonance (ESR) of hydrogen-like (shallow) impurities in covalent semiconductor crystals, beginning with the work of Wilson,[1] this subject still attracts much attention. In the last decade, a number of studies[2–5] were devoted to the low-temperature[6] (down to units of kelvin) magnetic susceptibility of crystalline semiconductors doped with hydrogen-like donors under the conditions of interaction of electron spins localized on donors, in particular on the insulator side of the concentration insulator–metal phase transition (Mott transition). The impurity diamagnetic susceptibility of a doped semiconductor close to this transition was experimentally determined for the first time[4] using a comparative study by the methods of superconducting quantum interference device (SQUID) magnetometry and ESR. It has been shown by ESR spectroscopy (see, e.g., Ref. 2 and an earlier work, Ref. 7) that in semiconductor crystals close to the Mott transition electrons with oppositely directed spins, which are weakly localized on the nearest impurities, may form the so-called antiferromagnetic spin glass. (On the other hand, the existence of the magnetic ordering in semiconductor materials and structures doped with shallow impurities is also

© Author(s) 2021

supported experimentally with the use of methods different from ESR.[8,9])

As was found using the ESR technique,[3,4] in the compensated n-Ge:As,Ga, which is close to the insulator–metal phase transition, the temperature decrease (below a few kelvin) leads to a transition from the Pauli paramagnetism[10] to the Curie paramagnetism, accompanied by an anomalous increase in the paramagnetic susceptibility and g-factor, which is characteristic of a magnetic transition. A qualitative model of this phenomenon was proposed[5] on the basis of the effect of localization of electron spins in the Coulomb gap, which arises due to the Coulomb blockade of electrons in a "metalized" impurity band under the field of compensating impurities at low temperatures corresponding to the thermal energy smaller than the gap width. Nevertheless, the question of the theoretical substantiation of possible types of magnetic ordering of shallow impurities in covalent diamagnetic semiconductors is still lacking.

In this paper, we propose a model for the transition from the antiferromagnetic ordering of electron spins of shallow paramagnetic impurities (donors) to the ferromagnetic ordering. This transition is affected by internal (doping level and degree of compensation) and external (temperature and magnetic field) factors. The model is based on the phenomenological theory of the molecular field (Weiss field)[11] for low temperatures, when the concentration of electrons in the states of the donor band is much higher than the concentration of electrons in the conduction band (c-band). Such a consideration is applicable for not too high doping levels (when the band of donor states is still separated by the gap from the bottom of the c-band) and the smallness of the average kinetic energy of a c-band electron compared to the average Coulomb energy of its attraction to the ionized donor.[12]

Let us consider a crystalline n-type diamagnetic covalent semiconductor with hydrogen-like impurities. The concentration of donors in the charge states (0) and $(+1)$ is $N = N_0 + N_{+1}$, and the concentration of acceptors, which are all in the charge state (-1), is KN; the charge states of impurities are expressed in units of the elementary charge e. It is assumed that the impurities are randomly (Poissonian) distributed over the crystal, and the electrical neutrality condition is satisfied, $N_{+1} = KN$, where $0 \le K \le 1$ is the compensation ratio.

In the phenomenological theory of the molecular field, the spin magnetic moment of an electron localized on a hydrogen-like impurity atom experiences an orienting effect not only from the external magnetic field with the induction $B_0 = \mu_0 H_0$, but also from, induced by the nearest spins, an effective "exchange" magnetic field with the strength

$$H_\mathrm{m} = B_\mathrm{m}/\mu_0 = \lambda M, \tag{1}$$

where μ_0 is the magnetic constant, λ is the coefficient of proportionality, and M is the total magnetic moment.

The intensity of the ESR signal of donors is proportional to the difference in the concentration of donors with the spin magnetic moments of electrons in the direction $(0\uparrow)$ and opposite to the direction $(0\downarrow)$ of the external magnetic field induction, i.e., $N_{0\uparrow} - N_{0\downarrow}$.

On the one hand, the total electron spin magnetic moment of all donors in the charge state (0) with spin S is given by the following formula:[13]

$$M = N_0 g_\mathrm{d} \mu_\mathrm{B} S B_S\left(\frac{g_\mathrm{d}\mu_\mathrm{B} B_0 S}{k_\mathrm{B} T}\right), \tag{2}$$

where $N_0 = N_{0\uparrow} + N_{0\downarrow} = (1-K)N$ is the concentration of donors in the charge state (0) at low temperatures, $g_\mathrm{d} \approx 1.57$ is the g-factor of an electron of the hydrogen-like donor impurity of arsenic in the germanium crystal, which is not involved in the covalent chemical bonding,[3] $B_0 = 425$ mT is the induction of the external constant magnetic field used in ESR experiments in Refs. 3–5, k_B is the Boltzmann constant, T is the absolute temperature, $k_\mathrm{B}T$ is the thermal energy, μ_B is the Bohr magneton, and $B_S(x)$ is the Brillouin function; $B_{1/2}(x) = \tanh x$ for $S = 1/2$.

On the other hand, the total electron spin magnetic moment of donors in the charge state (0) is determined by the number of uncompensated spin moments (see, e.g., Refs. 14 and 15),

$$M = \frac{g_\mathrm{d}\mu_\mathrm{B}(N_{0\uparrow} - N_{0\downarrow})}{2}. \tag{3}$$

Comparing Eq. (2), for $S = 1/2$, with Eq. (3), we get

$$N_{0\uparrow} - N_{0\downarrow} = N_0 \tanh\left(\frac{g_\mathrm{d}\mu_\mathrm{B} B_0}{2k_\mathrm{B} T}\right), \tag{4}$$

where $g_\mathrm{d}\mu_\mathrm{B}/2$ is the modulus of the magnetic moment of the donor electron in the charge state (0).

From Eq. (4), taking into account $N_{0\uparrow} + N_{0\downarrow} = N_0$, we obtain the concentration of electrically neutral donors with the electron spin directed along $(0\uparrow)$ and against $(0\downarrow)$ the field

$$\begin{aligned} N_{0\uparrow} &= \frac{N_0}{2}\left[1 + \tanh\left(\frac{g_\mathrm{d}\mu_\mathrm{B} B_0}{2k_\mathrm{B} T}\right)\right], \\ N_{0\downarrow} &= \frac{N_0}{2}\left[1 - \tanh\left(\frac{g_\mathrm{d}\mu_\mathrm{B} B_0}{2k_\mathrm{B} T}\right)\right]. \end{aligned} \tag{5}$$

To take into account the effective exchange magnetic field B_m acting on the electron spins of donors, in Eq. (4), we should write $B_0 + B_\mathrm{m}$ instead of B_0, so that

$$N_{0\uparrow} - N_{0\downarrow} = N_0 \tanh\left(\frac{g_\mathrm{d}\mu_\mathrm{B}(B_0 + B_\mathrm{m})}{2k_\mathrm{B} T}\right). \tag{6}$$

For weak magnetic fields ($g_\mathrm{d}\mu_\mathrm{B} B_0 \ll k_\mathrm{B} T$), confining ourselves to the first term in the expansion of $\tanh x$ in a series at $x \ll 1$ and passing, using the relations $B_0 = \mu_0 H_0$ and $B_\mathrm{m} = \mu_0 H_\mathrm{m}$, to the magnetic field strengths H_0 and H_m, from Eq. (6), we obtain

$$N_{0\uparrow} - N_{0\downarrow} = N_0 \frac{\mu_0 g_\mathrm{d}\mu_\mathrm{B}(H_0 + H_\mathrm{m})}{2k_\mathrm{B} T}. \tag{7}$$

Then, according to Eq. (3), taking into account Eqs. (1) and (7), the total magnetic moment of electrically neutral donors with uncompensated electron spin magnetic moments is

$$M = \frac{\mu_0 g_\mathrm{d}^2 \mu_\mathrm{B}^2 N_0}{4k_\mathrm{B} T}(H_0 + \lambda M). \tag{8}$$

From Eq. (8), it follows that

$$M = \frac{\mu_0 g_\mathrm{d}^2 \mu_\mathrm{B}^2 N_0 H_0}{4k_\mathrm{B} T - \mu_0 g_\mathrm{d}^2 \mu_\mathrm{B}^2 N_0 \lambda}. \tag{9}$$

© Author(s) 2021

Then, taking into account Eq. (9), the dimensionless paramagnetic susceptibility of electrically neutral donors is

$$\chi_{\rm d} = \frac{M}{H_0} = \frac{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0}{4k_{\rm B}T - \mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0 \lambda} = \frac{C}{T-\Theta}. \tag{10}$$

Here, the Curie constant C and the Curie–Weiss temperature Θ are given by the following relations:

$$C = \frac{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0}{4k_{\rm B}}, \quad \Theta = \frac{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0 \lambda}{4k_{\rm B}} = \lambda C, \tag{11}$$

where $\Theta > 0$, $\Theta = 0$, and $\Theta < 0$ correspond to the ferromagnetism, paramagnetism, and antiferromagnetism of the system of electron spins of donors in the charge state (0), respectively.

Note that the dimensionless quantity $\chi_{\rm d}$ according to Eq. (10) is written in SI units. The relationship between the value $[\chi_{\rm d}]_{\rm CGS}$, written in the CGS (Gaussian) system of units, and the value $[\chi_{\rm d}]_{\rm SI}$, written in the SI system, has the form:[16] $[\chi_{\rm d}]_{\rm SI} = 4\pi[\chi_{\rm d}]_{\rm CGS}$.

The purpose of this work is to describe the Curie–Weiss low-temperature behavior of the impurity paramagnetic susceptibility $\chi_{\rm d}$ in diamagnetic covalent semiconductors, doped with donors up to the insulator–metal phase transition, and to study the effect of the doping level and the degree of compensation on this behavior. First, we have found the relation between the strength of the effective internal magnetic field $H_{\rm m}$ and the total magnetic moment M of neutral donors. Then, the Curie–Weiss temperature Θ is calculated and its behavior is studied depending on the doping level and the degree of compensation. In conclusion, we discuss main results using the predictions of the proposed model to be compared with the experimental data on the n-Ge:As doped up to the metal–insulator phase transition and compensated by Ga acceptor impurities.

II. EFFECTIVE INTERNAL MAGNETIC FIELD STRENGTH

According to Ref. 11, the magnitude of the effective internal magnetic field of strength $\mathbf{H}_{\rm m}$ is found in a self-consistent way from the condition of the equality of the Heisenberg Hamiltonian $\mathcal{H}_{\rm H}$, containing this field inside the exchange integral, and the Hamiltonian of the Zeeman splitting $\mathcal{H}_{\rm Z}$ under this field. In our case, they can be represented as

$$\begin{aligned} \mathcal{H}_{\rm H} &= -2J\,\mathbf{S}_i \cdot \sum_{j=1}^{z} \mathbf{S}_j = -2zJ\,\mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle, \\ \mathcal{H}_{\rm Z} &= -\mu_0 g_{\rm d} \mu_{\rm B}\,\mathbf{S}_i \cdot \mathbf{H}_{\rm m}, \end{aligned} \tag{12}$$

where J is the exchange integral between a pair of the nearest-neighbor (first nearest) donors in the charge state (0), $\mathbf{S}_i$ is the spin moment of the donor in the charge state (0) with spin S_i (in units of the Planck constant $\hbar$), z is the number of the nearest neighbors (electrically neutral donors with an average spin moment $\langle \mathbf{S}_j \rangle$) for a given neutral donor with spin S_i.

Setting $\mathcal{H}_{\rm H} = \mathcal{H}_{\rm Z}$, according to Eq. (12), we find

$$\mathbf{H}_{\rm m} = \frac{2zJ}{\mu_0 g_{\rm d} \mu_{\rm B}} \langle \mathbf{S}_j \rangle. \tag{13}$$

Since the total magnetic moment is $\mathbf{M} = N_0 g_{\rm d} \mu_{\rm B} \langle \mathbf{S}_j \rangle$, and the strength of the internal magnetic field is $\mathbf{H}_{\rm m} = \lambda \mathbf{M}$, from Eq. (13), we obtain

$$\lambda = \frac{2zJ}{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0}. \tag{14}$$

Note that to calculate the value of J for the electron spins (quasi)localized on donors, one cannot use the formulas for the exchange energy of c-band electrons according to the model in Ref. 17. Moreover, within the framework of the Ising model, a numerical simulation of the direct exchange interaction of magnetic impurities (e.g., Mn) in nonmagnetic semiconductors was carried out recently in Ref. 18. It was shown in this work that at low temperatures, regardless of the sign of the value of the interimpurity exchange interaction (i.e., the sign of the J integral), the Curie law for the impurity magnetic susceptibility is not satisfied. The issue arises due to the formation of a spin glass phase by the uncompensated electron spins of impurities.

Substituting Eq. (14) for the proportionality coefficient λ (between the spin magnetic moment $\mathbf{M}$ of a set of electrically neutral donors and the strength of the internal magnetic field $\mathbf{H}_{\rm m}$) into Eq. (11), we obtain the Curie–Weiss temperature in the following form:

$$\Theta = \frac{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0}{4k_{\rm B}} \frac{2zJ}{\mu_0 g_{\rm d}^2 \mu_{\rm B}^2 N_0} = \frac{zJ}{2k_{\rm B}}, \tag{15}$$

where $z = 1$ is the number of donors in the charge state (0) nearest to the given donor, which is also in the charge state (0); the exchange integral J is calculated in Sec. IV.

III. HEITLER–LONDON MODEL FOR A PAIR OF ELECTRICALLY NEUTRAL DONORS

According to the Heitler–London model (see, e.g., Ref. 19), the solution of the Schrödinger equation for the H_2 molecule gives two energy levels (singlet and triplet) with the values specified only by the ionization energy of the hydrogen atom and the distance between two protons in this electroneutral molecule. Let us apply this approach to a system of two electrically neutral donors (and two electrons localized on them).

The singlet state of the system is characterized by symmetric spatial and antisymmetric spin wave functions (the product of a spatial wave function and a spin wave function should be antisymmetric due to the Pauli principle). The energy of the molecular system "two donors in the charge state (0)" in a singlet state is[20,21]

$$E_{\rm s}(\rho) = \frac{Q + A}{1 + S_{\rm d}^2}, \tag{16}$$

where

$$\begin{aligned} Q &= 2\overline{E}_{\rm d} \frac{1}{\rho}\left(1 + \frac{5}{8}\rho - \frac{3}{4}\rho^2 - \frac{1}{6}\rho^3\right)\exp(-2\rho), \\ A &= 2\overline{E}_{\rm d}\left\{\frac{S_{\rm d}^2}{\rho}\left[1 + \frac{6}{5}(\gamma + \ln\rho)\right]\right. \\ &\quad - \left(\frac{11}{8} + \frac{103}{20}\rho + \frac{49}{15}\rho^2 + \frac{11}{15}\rho^3\right)\exp(-2\rho) \\ &\quad \left. + \frac{6M_{\rm d}}{5\rho}\left[M_{\rm d}{\rm Ei}(-4\rho) - 2S_{\rm d}{\rm Ei}(-2\rho)\right]\right\}, \\ S_{\rm d} &= (1 + \rho + \rho^2/3)\exp(-\rho), \end{aligned}$$

© Author(s) 2021

where $\overline{E_d}$ is the average thermal ionization energy of a donor, which depends on the concentration of donors and acceptors; $\rho = r/a_H$ is the ratio of the distance r between the centers of two electrically neutral donors to the Bohr radius $a_H = e^2/8\pi\varepsilon_r\varepsilon_0 I_d$ for a single donor with the ionization energy I_d; e is the elementary charge; ε_r is the relative dielectric constant of the crystal matrix; ε_0 is the electric constant; $\gamma = 0.577\,22$ is the Euler constant; $M_d = (1 - \rho + \rho^2/3)\exp(\rho)$; $Ei(x) = -\int_{-x}^{\infty} t^{-1}\exp(-t)\,dt$ is an exponential integral function.[22]

The triplet state of the system "two donors in the charge state (0)" is described by the antisymmetric spatial and symmetric spin wave functions with the energy[20,21]

$$E_t(\rho) = \frac{Q - A}{1 - S_d^2}. \tag{17}$$

The difference in energies of the triplet (t) and singlet (s) states of electrons on a solitary pair of donors [both in the charge state (0)] according to Eqs. (16) and (17) is

$$\delta E_{0,0}(\rho) = E_t(\rho) - E_s(\rho) = \frac{2(QS_d^2 - A)}{1 - S_d^4}. \tag{18}$$

The effective width of the donor band[23] for a Gaussian distribution of donor energy levels relative to the energy level I_d of a single donor can be written as[24]

$$W_d = 2.64\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}(2KN)^{1/3}, \tag{19}$$

where $2KN$ is the total concentration of donor (N_{+1}) and acceptor (KN) ions at low temperatures (when $N_{+1} = KN$). When calculating W_d, only the Coulomb interaction of the nearest impurity ions randomly (Poissonian) distributed in the crystal was taken into account.

Note that, according to Refs. 24 and 25, at low temperatures, the concentration of c-band electrons is $n \ll K(1-K)N$ and the root-mean-square fluctuation of their potential energy $W_n \ll W_d$. The inequality $W_n \ll W_d$ is due to the fact that the "cold" electron is not affected by potential energy fluctuations on spatial scales smaller than its average wavelength (according to de Broglie), which is much greater than the average distance between impurity ions.

For a broad, in comparison with the thermal energy, donor band ($W_d \gg k_B T$), the average thermal ionization energy of the donor in the charge state (0) is determined by the following expression (see Ref. 26 and also Refs. 25 and 27 for an acceptor in a p-type crystal):

$$\overline{E_d} = I_d + \Delta_d + \delta E_c, \tag{20}$$

where $I_d = e^2/8\pi\varepsilon_r\varepsilon_0 a_H = 14.17$ meV is the thermal ionization energy of a single hydrogen-like donor (an As atom replacing a Ge atom in the crystal structure),[28] Δ_d is the shift of the Fermi level relative to the energy level I_d of a single donor, and $\delta E_c < 0$ is the shift of the bottom of the c-band to the bandgap (further calculated in two ways).[29]

For low temperatures, the quantity Δ_d is found from the equation of electrical neutrality of the covalent crystal: $N_{+1} = KN$, where $N_{+1} = N - N_0$ is the volume concentration of ionized donors and K is the ratio of the compensating impurity concentration to the main (dopant) impurity concentration. Thus, taking the Gaussian distribution of donor energy levels with respect to I_d, for $W_d \gg k_B T$, we obtain[27,30]

$$2K = 1 + \mathrm{erf}\left(\frac{\Delta_d}{\sqrt{2}W_d}\right), \tag{21}$$

where $\mathrm{erf}(\cdot)$ is the error function;[22] $W_d > 0$ is determined by Eq. (19); the quantity $\Delta_d < 0$ for $K < 0.5$, $\Delta_d = 0$ for $K = 0.5$, and $\Delta_d > 0$ for $K > 0.5$.

Note that the quantity Δ_d, according to Eq. (21), is determined by the concentration of donors N and the compensation ratio K. As formally follows from Eq. (21), for the limiting cases of the compensation ratios $K \to 0$ and $K \to 1$, the ratio $\Delta_d/W_d \to -\infty$ and $+\infty$, respectively.

The shift of the bottom of the c-band $\delta E_c < 0$ to the bandgap is calculated in the quasi-classical approximation of quantum mechanics accounting for two possible factors.

(i) Restriction of the region of electron localization on the donor,[31]

$$\delta E_{c1} = -I_d\frac{a_H}{R_{im}} < 0, \tag{22}$$

where $R_{im} = 0.62[(1+K)N]^{-1/3}$ is the average radius of a spherical region per impurity atom in a crystal matrix.

Formula (22) gives the value of the lowering of the bottom of the c-band to the bandgap ($\delta E_{c1} < 0$) due to collectivization of the excited states of donors in the charge state (0) and their merging with the c-band states with the donor concentration and the compensation ratio (due to decreasing R_{im}).

(ii) Screening (in the Debye–Hückel approximation) of the Coulomb field of an ionized donor by electrons hopping between donors in the charge states (0) and (+1) against the background of stationary negatively charged acceptor ions,[30,32]

$$\delta E_{c2} = -I_d\frac{3a_H}{2(\Lambda_{sc} + R_{im})} < 0, \tag{23}$$

where Λ_{sc} is the screening length (radius) of the impurity ion.

Formula (23) gives a decrease in the energy of the affinity of the c-band electron to the donor in the charge state (+1). The value of δE_{c2} is equal to the electrostatic energy of the electrically neutral system "donor ion + cloud of locally uncompensated negative charges screening it." The charge states of donors seem to migrate over the crystal due to hopping of electrons with the effective concentration[33] $N_0 N_{+1}/N = (1-K)KN$. In this case, acceptors are in the charge state (−1) and are immobile.

At low temperatures (when the donor bandwidth W_d is much greater than the thermal energy $k_B T$), the screening length Λ_{sc} is described by the following expression:[27,30]

$$\Lambda_{sc} = 0.814\frac{K^{1/6}}{N^{1/3}}\exp\left[\frac{1}{4}\left(\frac{\Delta_d}{W_d}\right)^2\right], \tag{24}$$

where the quantity Δ_d/W_d, for the known compensation ratio K of donors by acceptors, is found from Eq. (21).

© Author(s) 2021

From Eq. (24), taking into account Eq. (21), it follows that $\Lambda_{sc} \to \infty$ in the limiting cases $K \to 0$ and $K \to 1$, when the hopping migration of electrons between donors in the charge states (0) and (+1) is impossible (there are no free places or no electrons on donors, respectively). In this case, the effective concentration of electrons hopping between donors $(1-K)KN \to 0$. For $K = 0.5$, when $\Delta_d = 0$, the screening length is minimal: $\Lambda_{sc} = 0.725N^{-1/3}$.

By comparing Eqs. (22) and (23), we conclude that the shift of the bottom of the c-band $|\delta E_{c1}| > 0$ due to the restriction of the region of electron localization on each donor in the charge state (0) is greater than the shift of the bottom of the c-band $|\delta E_{c2}| > 0$ due to the screening of the Coulomb field of each donor in the charge state (+1).

Let us estimate the applicability of Eq. (20) taking into account Eqs. (21)–(23). So, according to Eq. (20), the value of $\overline{E_d}$ goes to zero for $K = 0.5$ ($\Delta_d = 0$) and $\delta E_c = \delta E_{c1}$ by Eq. (22) at the concentration of donors (arsenic atoms) $N_1 \approx 4.4 \cdot 10^{18}$ cm^{-3}, while for $\delta E_c = \delta E_{c2}$ by Eq. (23)—at the donor concentration $N_2 \approx 1.7 \cdot 10^{19}$ cm^{-3}. Let us now compare the values of the concentrations N_1 and N_2 with the critical concentration of arsenic $N = N_M$, corresponding to the transition of a germanium crystal from the insulator state to the metallic one (the Mott transition).

According to Ref. 34, the quantity N_M is determined by the relation

$$N_M^{1/3} a_H = \frac{0.542}{[(1-K)(\varepsilon_r + 2)]^{1/3}}, \tag{25}$$

where $\varepsilon_r = 15.4$ is the low-temperature low-frequency relative permittivity of the germanium crystal.[35]

Calculations using Eq. (25) are in general quantitatively consistent[34] with the experimental data for n- and p-type silicon and germanium crystals doped with hydrogen-like impurities over a wide range of dopant concentrations and compensation ratios. As follows from Eq. (25), for n-Ge:As,Ga at $K = 0.5$, the calculated critical concentration of arsenic is $N_M \approx 5.1 \cdot 10^{17}$ cm^{-3}. [The experimental value is $N_M \approx 3.7 \cdot 10^{17}$ cm^{-3} for $K \to 0$ (see Ref. 34 and references therein).] It is evident that the values N_1 and N_2 obtained from the condition $\overline{E_d} = 0$ for $\delta E_c = \delta E_{c1}$ by Eq. (22) and for $\delta E_c = \delta E_{c2}$ by Eq. (23) considerably exceed the value of the critical concentration N_M from Eq. (25). In other words, the insulator–metal concentration phase transition occurs in the donor band, before it merges with the bottom of the c-band. This was experimentally shown for the first time in Ref. 36, which played an important role in the formation of ideas about the Mott transition upon doping and compensation of semiconductors (see also Ref. 37).

IV. CALCULATIONS OF EXCHANGE INTEGRAL AND CURIE–WEISS TEMPERATURE

The probability that an impurity atom randomly selected among all the impurity atoms is a donor in the charge state (0) is $(1-K)/(1+K)$. The fractions of neutral donors having the magnetic moment oriented along and against the direction of the external magnetic field are $N_{0\uparrow}/N_0$ and $N_{0\downarrow}/N_0$, respectively. We assume that donors in the charge states (0) and (+1), as well as acceptors in the charge state (−1), are randomly distributed over the crystal (specifically, with the Poisson distribution; see, e.g., Refs. 24 and 38). In this approximation, the probability $\mathcal{P}_{0,0}(\rho)\,\mathrm{d}\rho$ that two donors are the nearest-neighbor electrically neutral donors is the product of three probabilities: (i) the probability $4\pi a_H^3 \rho^2 (1-K)N\,\mathrm{d}\rho$ to find a donor in the charge state (0) in a spherical layer with radius $r = a_H\rho$ and thickness $\mathrm{d}r = a_H \mathrm{d}\rho$, (ii) the probability $(1-K)/(1+K)$ that an impurity atom in the center of the sphere is a donor in the charge state (0), and (iii) the probability $\exp[-(4\pi/3)(a_H\rho)^3(1-K)N]$ that there are no other donors in the charge state (0) in a ball of radius r, that is,

$$\mathcal{P}_{0,0}(\rho)\,\mathrm{d}\rho = \frac{1-K}{1+K} 4\pi a_H^3 \rho^2 (1-K)N \times \exp\left(-\frac{4\pi}{3}(a_H\rho)^3(1-K)N\right)\mathrm{d}\rho. \tag{26}$$

The exchange integral J in Eq. (15) is found as the average exchange energy per two nearest (the first nearest) electrically neutral donors in a germanium crystal,

$$J = \frac{1}{N_0^2}\left[\left(N_{0\uparrow}^2 + N_{0\downarrow}^2\right)\overline{E_t} + 2N_{0\uparrow}N_{0\downarrow}\overline{E_s}\right], \tag{27}$$

where $N_0^2 = (N_{0\uparrow} + N_{0\downarrow})^2 = N_{0\uparrow}^2 + 2N_{0\uparrow}N_{0\downarrow} + N_{0\downarrow}^2$; the quantities $N_{0\uparrow}$ and $N_{0\downarrow}$ are determined according to Eq. (5); $\overline{E_t}$ and $\overline{E_s}$ are the average energies of the triplet (t) by Eq. (17) and singlet (s) by Eq. (16) states of electrons on a pair of donors in the charge state (0). The quantities $\overline{E_t}$ and $\overline{E_s}$ are calculated as follows:

$$\begin{aligned} \overline{E_t} &= \int_0^\infty E_t(\rho)\,\mathcal{P}_{0,0}(\rho)\,\mathrm{d}\rho, \\ \overline{E_s} &= \int_0^\infty E_s(\rho)\,\mathcal{P}_{0,0}(\rho)\,\mathrm{d}\rho, \end{aligned} \tag{28}$$

where $\mathcal{P}_{0,0}(\rho)$ is given by Eq. (26).

Note that in Eq. (27), the ratios $(N_{0\uparrow}/N_0)^2$ and $(N_{0\downarrow}/N_0)^2$ are the probabilities that both of the nearest donors in the charge state (0) have spins co-directed and oppositely directed to the induction of an external field, respectively (i.e., they are in the triplet state), and $2N_{0\uparrow}N_{0\downarrow}/N_0^2$ is the probability that the electron spins in a pair of the nearest donors in the charge state (0) are oppositely directed (i.e., they are in a singlet state). The values of $E_s(\rho)$ and $E_t(\rho)$ are calculated by Eqs. (16) and (17), respectively.

The signs of the terms inside the square bracket in Eq. (27) are chosen in such a way that in the triplet state the energy of the system of two electrons is higher than in the singlet state.[39]

We consider an n-type germanium doped with arsenic atoms and compensated with gallium atoms on the insulator side close to the Mott transition. Let us estimate the characteristic temperature T_m, below which it is possible to observe the magnetic ordering of donors in the charge state (0) with uncompensated electron spin magnetic moments. We assume that for the manifestation of spin ordering, it is necessary that the average acoustic phonon energy $\overline{E_{ac}}$ does not exceed the average splitting between the triplet and singlet states $|\overline{E_t} - \overline{E_s}|$ of a pair of the nearest donors in the charge state (0). It can be shown (following, e.g., Refs. 40 and 41) that at temperatures much lower than the Debye temperature in germanium crystals ($T_D = 374$ K; see Ref. 28), the average acoustic phonon energy in the Debye approximation equals $\overline{E_{ac}} = (\pi^4/36)k_B T_m$.

© Author(s) 2021

Then, taking into account $\overline{E_{ac}} \le |\overline{E_t} - \overline{E_s}|$ and Eq. (28), the temperature T_m is determined by the following relation:

$$T_m \le \frac{36}{\pi^4 k_B} |\overline{E_t} - \overline{E_s}| = \frac{36}{\pi^4 k_B} \int_0^\infty |\delta E_{0,0}(\rho)| \, \mathcal{P}_{0,0}(\rho) \, d\rho, \qquad (29)$$

where $\mathcal{P}_{0,0}(\rho)$ is given by Eq. (26); the quantity $\delta E_{0,0}(\rho)$ is determined by Eq. (18). For $T \ll T_D$, the concentration of acoustic phonons is $N_{ac} \approx 21.6 N_{Ge}(T/T_D)^3$, where $N_{Ge} \approx 4.4 \cdot 10^{22}$ cm^{-3} is the concentration of intrinsic atoms in a germanium crystal. For $T = 4.2$ K, we have $N_{ac} \approx 1.35 \cdot 10^{18}$ cm^{-3}, which slightly exceeds the critical concentration of donors in germanium for the insulator–metal transition [see Refs. 3 and 4 and Eq. (25)].

Figure 1 shows the calculated Curie–Weiss temperature Θ and specific paramagnetic susceptibility χ_d/d_{Ge} of n-Ge:As,Ga crystals as a function of the dopant (arsenic) concentration N for the compensation ratio $K = 0.5$ (which turns out to be optimal for the manifestation of ferromagnetic spin ordering) and the temperature $T = 3$ K; the density of germanium is $d_{Ge} = 5.3234$ g/cm^3 (see Ref. 28). It can be seen that at doping levels considerably lower than the critical values for the insulator–metal transition, the Curie–Weiss temperature falls to the region of ultralow temperatures below 1 K, while the deviations from the Curie law are insignificant. This creates particular difficulties during experimental studies of the phenomena associated with electron spins.

Figure 2 shows the calculated Curie–Weiss temperature Θ and specific paramagnetic susceptibility χ_d/d_{Ge} as a function of the compensation ratio K for the concentration of arsenic atoms $N = 3 \cdot 10^{17}$ cm^{-3} and $T = 3$ K. It can be seen that the model predicts sign changing of the Curie–Weiss temperature from minus to plus (low-temperature transition from antiferromagnetic to ferromagnetic local ordering of impurity spins) in the region of 15%–30%

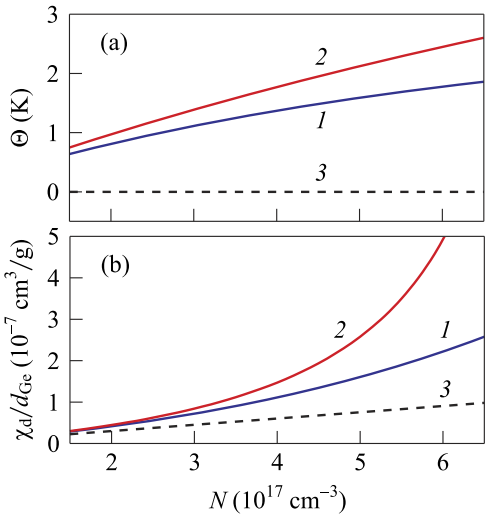


FIG. 1. Calculated Curie–Weiss temperature Θ (a) and specific paramagnetic susceptibility χ_d/d_{Ge} of hydrogen-like donors (b) as a function of the concentration of arsenic atoms N in the n-Ge:As,Ga crystal for the compensation ratio $K = 0.5$ at $T = 3$ K. Solid lines: calculations of Θ by Eq. (15) and χ_d/d_{Ge} by Eq. (10) taking into account δE_c by Eq. (22) (curve *1*) and δE_c by Eq. (23) (curve *2*); dashed line *3* is the Curie law ($\Theta = 0$ K).

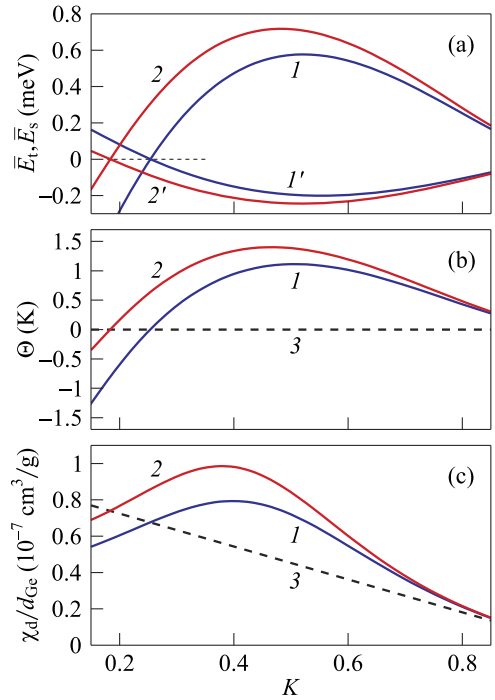


FIG. 2. Calculated average energies of triplet and singlet states $\overline{E_t}$ and $\overline{E_s}$ (a), Curie–Weiss temperature Θ (b), and specific paramagnetic susceptibility of hydrogen-like donors χ_d/d_{Ge} (c) as a function of the compensation ratio K in the n-Ge:As,Ga crystal with the concentration of arsenic atoms $N = 3 \cdot 10^{17}$ cm^{-3} at $T = 3$ K. Solid lines: calculations of $\overline{E_t}$ (*1*, *2*) and $\overline{E_s}$ (*1′*, *2′*) by Eq. (28), Θ by Eq. (15) and χ_d/d_{Ge} by Eq. (10) taking into account δE_c by Eq. (22) (curve *1*), and δE_c by Eq. (23) (curve *2*); dashed line *3* is the Curie law ($\Theta = 0$ K).

compensations, reaching (close to half compensations) the maximum positive values $\Theta \approx 1.3$ K with the following decrease (transition to paramagnetism) in the region of high compensations, when the spin exchange is weakened. The change in the sign of the Curie–Weiss temperature is associated with the change in the sign of the difference between the average energies of triplet and singlet states $\overline{E_t}$ and $\overline{E_s}$ [Fig. 2(a)] at relatively small compensation ratios of the order of ten percent.

V. COMPARISON WITH EXPERIMENT FOR COMPENSATED GERMANIUM

Figure 3 shows (in SI units) the temperature dependences for the specific paramagnetic susceptibility χ_d/d_{Ge} of compensated n-Ge crystals, where $d_{Ge} = 5.3234$ g/cm^3. Points represent the ESR measurements from Ref. 5 at $B_0 = 425$ mT of the magnetic susceptibility of n-Ge:As,Ga samples with the arsenic concentration $N = (3.97–4.49) \cdot 10^{17}$ cm^{-3}, compensated by gallium atoms with the compensation ratio $K = 0.28–0.58$. Solid lines are calculations for $N = 4.33 \cdot 10^{17}$ cm^{-3} and $K = 0.49$ according to Eq. (10) taking into account δE_c by Eq. (22) (curve *1*) and δE_c by Eq. (23) (curve *2*). Dashed line *3* indicates a calculation of the paramagnetic susceptibility according to Eq. (10) at $\Theta = 0$ K (Curie law) for the same values of N and K.

© Author(s) 2021

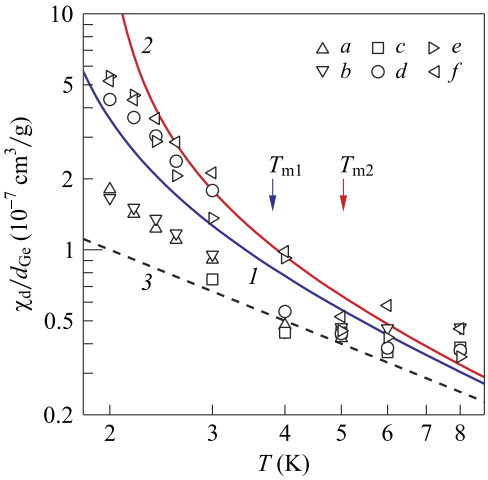


FIG. 3. Temperature dependence of the specific magnetic susceptibility χ_d/d_{Ge} of donors (electrically neutral arsenic atoms) in an *n*-Ge:As,Ga crystal with the donor concentration (in units of 10^{17} cm^{-3}) $N = 3.97$ (*a*), 4.24 (*b*), 4.36 (*c*), 4.46 (*d*), 4.48 (*e*), and 4.49 (*f*) and the compensation ratio $K = 0.28$ (*a*), 0.44 (*b*), 0.51 (*c*), 0.56 (*d*), 0.57 (*e*), and 0.58 (*f*); crystal density $d_{Ge} = 5.3234$ g/cm^3. The experimental points are taken from Ref. 5. Solid lines are calculations according to Eq. (10) for average values $N = 4.33 \cdot 10^{17}$ cm^{-3} and $K = 0.49$ taking into account Θ by Eq. (15), J by Eqs. (27) and (28) for $B_0 = 425$ mT, E_s and E_t by Eqs. (16) and (17), $\overline{E_d}$ by Eq. (20), δE_c by Eq. (22) (curve *1*), and δE_c by Eq. (23) (curve *2*); dashed line *3* is the calculation according to Eq. (10) for the average value $N_0 = (1 - K)N = 2.2 \cdot 10^{17}$ cm^{-3} at $\Theta = 0$ K (Curie law); the arrows show the temperatures T_{m1} and T_{m2} according to Eq. (29) taking into account δE_c by Eqs. (22) and (23), respectively.

Note that according to Eq. (19), for the donor concentration $N = 4.33 \cdot 10^{17}$ cm^{-3} and the compensation ratio $K = 0.49$, the impurity bandwidth W_d is equal to 18.5 meV. Thus, for $T = 3$ K, we have $W_d/k_BT \approx 72$, i.e., relation (21) is valid.

As seen, the Curie–Weiss behavior of the paramagnetic susceptibility predicted by the proposed model has a fairly good quantitative agreement with the experimental data from Refs. 2–5 for the samples of compensated *n*-Ge:As,Ga close to the insulator–metal phase transition. Note an agreement of the functional dependence on the compensation ratio, for which the proposed model predicts maximal values of χ_d at the compensation ratios ≈40%–50% (for $N = 3 \cdot 10^{17}$ cm^{-3}).

Thus, the constructed model provides the behavior of specific paramagnetic susceptibility χ_d/d_{Ge} that corresponds to the transition from the Curie law to the Curie–Weiss law (Curie–Weiss behavior) at temperatures below T_m.

The experiment (see Ref. 5) shows that the increase in paramagnetic susceptibility observed with a decrease in temperature from 5 to 3 K at lower temperatures ceases and it is replaced by the Curie law for electrons localized in the donor band, and at higher temperatures it transforms into a temperature-independent plateau (Pauli paramagnetism). Such a behavior is caused by the formation of a narrow Coulomb gap in the compensated samples on the insulator side of the insulator–metal phase transition. At temperatures higher than the Coulomb gap width, the gap does not manifest itself in the spin and transport properties. At even higher temperatures, when the energy distribution of electrons covers also the *c*-band states (electrons are not degenerate), the Curie law is observed again.

VI. CONCLUSION

The antiferromagnet–ferromagnet–paramagnet transition of a diamagnetic semiconductor doped with paramagnetic hydrogen-like donors is described theoretically for the first time as a function of the temperature T and the compensation ratio K. (For an *n*-type semiconductor, the quantity K is the ratio of the concentration of compensating acceptors KN to the concentration of doping donors N.) The Curie–Weiss behavior of the low-temperature paramagnetic susceptibility of compensated semiconductors on the insulator side of the insulator–metal phase transition is shown. For the analytical specification of the density of states in the impurity band, we used model concepts developed so far only for moderately doped semiconductors.

Calculations of the energy of exchange interaction of two electrons localized on the nearest two neutral donors are based on the Heitler–London model. Additionally, the shift of the bottom of the *c*-band to the bandgap is taken into account due to the separate influence of two factors: (i) due to confinement (limitation of the localization region) of the electron on the donor and (ii) due to screening of the Coulomb field of the donor ion by electrons hopping between hydrogen-like donors.

The model shows that the magnetic susceptibility satisfies the Curie–Weiss law with the Curie–Weiss temperature, which grows with compensation, changes sign from minus to plus in the compensation region of 15%–30%, and then reaches values on the order of several kelvin at compensations of about 50% for doping levels in Ge close to the insulator–metal phase transition.

The applicability of the model to the experimental results obtained using the ESR spectroscopy technique requires a small Zeeman splitting of donor energy levels in the magnetic field with induction $B_0 = 425$ mT in comparison with the thermal energy.

The behavior of the paramagnetic susceptibility predicted by the model at low temperatures ($T \approx 2$–7 K) is in good agreement with the results of measurements performed using the ESR technique on a series of samples of compensated *n*-Ge:As,Ga close to the insulator–metal phase transition.

However, considering the experimental data on the magnetic susceptibility behavior in a wider temperature range (see Ref. 5), a qualitative difference is also seen. In experiments, for the temperatures $T > 7$ K, insulating (at lower temperatures) samples show a distinct transition to the Pauli paramagnetism, which is characteristic for "metalized electronic states" of the donor band. This is associated with the disappearance of the manifestation of a narrow Coulomb gap at the Fermi level in the donor band when the thermal energy is comparable to the width of this band. More precisely, at higher temperatures, when electrons pass from the states of the donor band to the *c*-band, the Curie paramagnetism gives way to the Pauli paramagnetism. The proposed model is limited to considerably lower temperatures at which both of the thermal effects indicated here do not occur.

© Author(s) 2021

ACKNOWLEDGMENTS

This work was supported by the Belarusian National Research Program "Materials Science, New Materials and Technologies" and by the Belarusian Republican Foundation for Fundamental Research (Grant No. F21RM-137).

The authors declare no competing financial interest.

DATA AVAILABILITY

The data that support the findings of this study are openly available in Mendeley Data at http://doi.org/10.17632/vmkywd69cr, Ref. 42.

REFERENCES

[1] D. K. Wilson, "Electron spin resonance experiments on shallow donors in germanium," Phys. Rev. **134**, A265–A286 (1964).

[2] A. I. Veinger, A. G. Zabrodskii, T. V. Tisnek, and S. I. Goloshchapov, "Antiferromagnetic spin glass ordering in the compensated *n*-Ge near the insulator–metal transition," Phys. Status Solidi C **1**, 71–74 (2004).

[3] A. I. Veinger, A. G. Zabrodskii, T. L. Makarova, T. V. Tisnek, S. I. Goloshchapov, and P. V. Semenikhin, "Low-temperature variation of magnetic order in a non-magnetic *n*-Ge:As semiconductor in the vicinity of the metal-insulator phase transition," J. Exp. Theor. Phys. **116**, 796–799 (2013) [Zh. Eksp. Teor. Fiz. **143**, 918 (2013)].

[4] A. I. Veinger, A. G. Zabrodskii, T. L. Makarova, T. V. Tisnek, S. I. Goloshchapov, and P. V. Semenikhin, "Detection of impurity diamagnetic susceptibility and its behavior in *n*-Ge:As in the region of the insulator–metal phase transition," Semiconductors **49**, 1294–1301 (2015) [Fiz. Tekh. Poluprovodn. **49**, 1339 (2015)].

[5] A. Zabrodskii, A. Veinger, and P. Semenikhin, "Effect of compensation on low-temperature spin ordering in Ge:As semiconductor near the insulator–metal phase transition," Appl. Magn. Reson. **51**, 327–347 (2020).

[6] At low temperatures, the average kinetic energy of electrons in the *c*-band is much less than the thermal ionization energy of the impurity, and they turn out to be "frozen out" to the states of the donor band.

[7] M. A. Paalanen, S. Sachdev, R. N. Bhatt, and A. E. Ruckenstein, "Spin dynamics of nearly localized electrons," Phys. Rev. Lett. **57**, 2061–2064 (1986).

[8] A. G. Andreev, S. V. Egorov, A. G. Zabrodskii, R. V. Parfen'ev, and A. V. Chernyaev, "Hysteresis of magnetoresistance in neutron-transmutation-doped Ge in the region of hopping transport over the Coulomb-gap states," Semiconductors **34**, 768–774 (2000) [Fiz. Tekh. Poluprovodn. **34**, 796 (2000)].

[9] V. M. Pudalov, "Measurements of the magnetic properties of conduction electrons," Phys.-Usp. **64**, 3–27 (2021) [Usp. Fiz. Nauk **191**, 3 (2021)].

[10] A. Zabrodskii, A. Veinger, and P. Semenikhin, "Anomalous manifestation of Pauli paramagnetism and Coulomb blockade of spin exchange upon the compensation of doped semiconductors," Phys. Status Solidi B **257**, 1900249 (2020).

[11] J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, 1966).

[12] N. A. Poklonski, S. A. Vyrko, O. N. Poklonskaya, and A. G. Zabrodskii, "Transition temperature from band to hopping direct current conduction in crystalline semiconductors with hydrogen-like impurities: Heat versus Coulomb attraction," J. Appl. Phys. **110**, 123702 (2011).

[13] S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, New York, 2001).

[14] S. V. Vonsovskii, *Magnetism* (Wiley, New York, 1974) in 2 vols.

[15] N. Majlis, *The Quantum Theory of Magnetism* (World Scientific, Singapore, 2007).

[16] R. B. Goldfarb, "Electromagnetic units, the Giorgi system, and the revised international system of units," IEEE Magn. Lett. **9**, 1205905 (2018).

[17] O. V. Konstantinov, O. I. Obolenskii, and B. V. Tsarenkov, "Exchange energy of a free electron in a semiconductor," Semiconductors **31**, 484–488 (1997) [Fiz. Tekh. Poluprovodn. **31**, 571 (1997)].

[18] N. A. Bogoslovskiy, P. V. Petrov, and N. S. Averkiev, "The impurity magnetic susceptibility of semiconductors in the case of direct exchange interaction in the Ising model," Phys. Solid State **61**, 2005–2009 (2019) [Fiz. Tverd. Tela **61**, 2036 (2019)].

[19] Y. Sugiura, "Über die Eigenschaften des Wasserstoffmoleküls im Grundzustande," Z. Phys. **45**, 484–492 (1927).

[20] A. S. Davydov, *Quantum Mechanics* (Pergamon Press, Oxford, 1976).

[21] L. A. Blumenfeld and A. K. Kukushkin, *The Course of Quantum Chemistry and Molecular Structure* (Moscow State University, Moscow, 1980) (in Russian).

[22] G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers: Definitions, Theorems, and Formulas for Reference and Review* (Dover, New York, 2000).

[23] We consider the case of the classical broadening of the donor band, when the spread of the donor energy levels due to the Coulomb interaction of the nearest impurity ions is much greater than the quantum broadening of their energy levels due to the finite time of electron localization on the donor.

[24] N. A. Poklonski, S. A. Vyrko, O. N. Poklonskaya, and A. G. Zabrodskii, "Role of electrostatic fluctuations in doped semiconductors upon the transition from band to hopping conduction (by the example of *p*-Ge:Ga)," Semiconductors **50**, 722–734 (2016) [Fiz. Tekh. Poluprovodn. **50**, 738 (2016)].

[25] N. A. Poklonski, S. A. Vyrko, O. N. Poklonskaya, A. I. Kovalev, and A. G. Zabrodskii, "Ionization equilibrium at the transition from valence-band to acceptor-band migration of holes in boron-doped diamond," J. Appl. Phys. **119**, 245701 (2016).

[26] N. A. Poklonski, S. A. Vyrko, and A. N. Dzeraviaha, "Thermal ionization energy of hydrogen-like impurities in semiconductor materials," J. Belarusian State Univ. Phys. **2**, 28–41 (2020) (in Russian).

[27] N. A. Poklonski, S. A. Vyrko, A. I. Kovalev, and A. N. Dzeraviaha, "Drift-diffusion model of hole migration in diamond crystals via states of valence and acceptor bands," J. Phys. Commun. **2**, 015013 (2018).

[28] O. Madelung, *Semiconductors: Data Handbook* (Springer, Berlin, 2004).

[29] The change in the thermal ionization energy of a donor (As) in germanium crystals under the magnetic field with induction B_0 = 425 mT can be neglected.

[30] N. A. Poklonski, S. A. Vyrko, and A. G. Zabrodskii, "Quasiclassical description of the nearest-neighbor hopping dc conduction via hydrogen-like donors in intermediately compensated GaAs crystals," Semicond. Sci. Technol. **25**, 085006 (2010).

[31] N. A. Poklonski, S. A. Vyrko, A. I. Kovalev, and A. G. Zabrodskii, "A quasi-classical model of the Hubbard gap in lightly compensated semiconductors," Semiconductors **50**, 299–308 (2016) [Fiz. Tekh. Poluprovodn. **50**, 302 (2016)].

[32] N. A. Poklonskii, A. I. Syaglo, and G. Biskupski, "A model of how the thermal ionization energy of impurities in semiconductors depends on their concentration and compensation," Semiconductors **33**, 402–406 (1999) [Fiz. Tekh. Poluprovodn. **33**, 415 (1999)].

[33] N. A. Poklonski and V. F. Stelmakh, "Screening of electrostatic fields in crystalline semiconductors by electrons hopping over defects," Phys. Status Solidi B **117**, 93–99 (1983).

[34] N. A. Poklonski, S. A. Vyrko, and A. G. Zabrodskii, "Electrostatic models of insulator–metal and metal–insulator concentration phase transitions in Ge and Si crystals doped by hydrogen-like impurities," Phys. Solid State **46**, 1101–1106 (2004) [Fiz. Tverd. Tela **46**, 1071 (2004)].

[35] T. G. Castner, N. K. Lee, H. S. Tan, L. Moberly, and O. Symko, "The low-frequency, low-temperature dielectric behavior of *n*-type germanium below the insulator-metal transition," J. Low Temp. Phys. **38**, 447–473 (1980).

[36] M. N. Alexander and D. F. Holcomb, "Semiconductor-to-metal transition in *n*-type group IV semiconductors," Rev. Mod. Phys. **40**, 815–829 (1968).

[37] P. P. Edwards, M. T. J. Lodge, F. Hensel, and R. Redmer, ". . .a metal conducts and a non-metal doesn't," Philos. Trans. R. Soc., A **368**, 941–965 (2010).

[38] P. G. Baranov, A. N. Ionov, I. V. Il'in, P. S. Kop'ev, E. N. Mokhov, and V. A. Khramtsov, "Electron paramagnetic resonance in neutron-transmutation-doped semiconductors with a changed isotopic composition," Phys. Solid State **45**, 1030–1041 (2003) [Fiz. Tverd. Tela **45**, 984 (2003)].

[39] When calculating the energy of exchange interaction for ferromagnets, the order of signs is chosen the same as in Eq. (27); see, e.g., P. G. Steeneken, "New light on EuO thin films: Preparation, transport, magnetism and spectroscopy of a ferromagnetic semiconductor," Ph.D. thesis, Rijksuniversiteit Groningen, Groningen, 2002.

© Author(s) 2021

[40]C. Kittel and H. Kroemer, *Thermal Physics* (W. H. Freeman, New York, 1980).
[41]N. A. Poklonski, S. A. Vyrko, and S. L. Podenok, *Statistical Physics of Semiconductors* (KomKniga, Moscow, 2005) (in Russian).
[42]N. A. Poklonski, S. A. Vyrko, A. N. Dzeraviaha, A. G. Zabrodskii, A. I. Veinger, and P. V. Semenikhin, "Data for: Curie-Weiss behavior of the low-temperature paramagnetic susceptibility of semiconductors doped and compensated with hydrogen-like impurities," Mendeley Data (2021).

© Author(s) 2021