

Effect of thermodynamic fluctuations of magnetization on the bound magnetic polaron state in ferromagnetic semiconductors

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Abstract

We extend the theory of the bound magnetic polaron (BMP) in diluted paramagnetic semiconductors to the situation with a ferromagnetic phase transition. This is achieved by including the classical Gaussian fluctuations of magnetization from the quartic (non-Gaussian) term in the effective Ginzburg–Landau Hamiltonian for the spins. Within this approach, we find a ferromagnetically ordered state within the BMP in the temperature range well above the Curie temperature for the host magnetic semiconductor. Numerical results are compared directly with the recently available experimental data for the ferromagnetic semiconductor GdN. The agreement is excellent, given the simplicity of our model, and is because the polaron size (≈ 1.4 nm) encompasses a relatively large but finite number ($N \approx 400$) of quasiclassical spins $S = 7/2$ coming from Gd^{3+} ions. The presence of BMP invalidates the notion of critical temperature and thus makes the incorporation of classical Gaussian fluctuations sufficient to realistically describe the situation.

Keywords: bound magnetic polaron, ferromagnetic semiconductors, magnetic properties of BMP



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1. Introduction

The properties of a shallow donor electron or acceptor hole in the presence of localized $3d$ or $4f$ electrons (termed throughout the paper as the spins) have been studied intensively experimentally [1–7] and theoretically [7–18] during the last four decades. The resultant bound state, for which both the electrostatic and the magnetic energy contributions are important, is called a bound magnetic polaron (BMP). These studies elucidated the role of the $s - d$ ($s - f$) exchange coupling of individual carriers to the non-uniformly distributed localized magnetic moments. More recently, the important role of these quantum systems has been discussed for materials encompassing diluted magnetic semiconductors, [19–23], ferromagnetic perovskites [24], and ferromagnetic semiconductors [25, 26]. BMPs, being objects of nanoscale size, have attracted a growing interest in the studies of various quantum structures [27–33]. The origin of ferromagnetism in DMSs [34–38] represents a basic question about the dominant role of antiferromagnetic superexchange in all of those materials when the carrier concentration is zero or small. Within a semiclassical approximation to the spins, one can consider even the limiting case of magnetic ions concentration $x = 1$ and thus encompass the limit of a ferromagnetic semiconductor. This, in turn, allows us to address the question of the validity of results for DMSs concerning BMP states also in the ferromagnetic phase. In this manner, one can question the validity of the results coming from the mean-field theoretical treatment developed by Kuivalainen *et al* [10], which have shown the appearance of the spin polarization within the BMP orbit at temperatures well above the critical temperature T_c of the host ferromagnetic semiconductor. The same effect, though not in such a clear form, has been observed in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [24]. One should also mention precursory theoretical studies [39] on autolocalization of the conduction band electrons due to magnetization fluctuations.

The purpose of this work is to address these important issues. To do this, we extend essentially a single BMP theory applicable to a paramagnetic DMS, developed by Dietl and Spalek (DS) [11] and others [12–17], to be applicable to a magnetic semiconductor with the ferromagnetic phase-transition (Curie) point. This is achieved by including the quartic term in magnetization in the system free energy functional for the spins. Within this approach, incorporating the effective Gaussian fluctuations around the mean-field ordered state, we also find a magnetically ordered ground state of the BMP in a temperature range well above the Curie–Weiss temperature of the host magnetic semiconductor. Our findings are quantitatively consistent with the experimentally observed magnetization [25, 26], as well as with previous theoretical investigations [10, 39]. Numerical calculations are presented for the values of material parameters corresponding to GdN and compared directly to recent experimental data [26].

The structure of the paper is as follows. In section 2 we formulate the theoretical approach with inclusion of fluctuations of magnetization due to the localized spins. In section 3 we compare the numerical analysis with experimental data in a quantitative manner. In section 4 we overview the entire approach. In appendix A, we provide a brief overview of the derivation of the effective Ginzburg–Landau (G–L) functional for the spins and estimate its parameters.

2. Theory

2.1. Effective Hamiltonian with fluctuating variables

We start by considering a ferromagnetic crystal consisting of equal-magnitude localized magnetic moments distributed over lattice sites $\{i\}$, each possessing spin $S_i = S$. Magnetic properties of the host spins are described by the Heisenberg Hamiltonian and, for the sake of simplicity, we limit ourselves to the magnetic ions with quenched orbital moment, $L = 0$. The system also contains isolated shallow donors with electronic states that are described with the help of the effective mass approximation. With this formulation, the model has quite a wide range of applications, e.g., BMPs in ferromagnetic semiconductors, insulators, or DMSs, provided that the distance between the donors is substantially larger than their hydrogenic-like orbital size. Furthermore, within the continuous-medium approximation for the spins, one can write the donor electron Hamiltonian in the form [11]

$$\mathcal{H}_e \varphi_\sigma(\mathbf{r}) = \mathcal{H}_1 \varphi_\sigma(\mathbf{r}) - \frac{1}{2} \boldsymbol{\sigma} \cdot \boldsymbol{\Delta}[\mathbf{M}; \varphi], \quad (1)$$

where \mathcal{H}_1 is the single-particle part of the Hamiltonian and the polaron effective spin splitting $\boldsymbol{\Delta}[\mathbf{M}; \varphi]$ is defined as follows:

$$\boldsymbol{\Delta}[\mathbf{M}; \varphi] \equiv g^* \mu_B \mathbf{H}_a - J_c \hat{\mathbf{S}}(\mathbf{r}), \quad (2)$$

where g^* is the Landé factor for the donor electron, \mathbf{H}_a is the applied magnetic field, $\boldsymbol{\sigma}$ denotes the Pauli matrices, and J_c is the exchange integral of the contact Fermi (s - d (f)) interaction between localized spins $\{\hat{\mathbf{S}}_i\}$ and those of impurity carrier $\hat{\mathbf{S}}_j$. The spin density is defined as $\hat{\mathbf{S}}(\mathbf{r}) \equiv \sum_i \hat{\mathbf{S}}_i \delta(\mathbf{r} - \mathbf{r}_i)$, with the summation running over the sites occupied by the magnetic ions.

The assumptions that the exchange field is weak and that orbital moments are absent (as for e.g., Mn^{2+} or Eu^{2+} ions) allow us to write the electron wave function as a product of functions that depend on the spatial and the spin variables separately:

$$\Psi\left(\{\hat{\mathbf{S}}_i\}; \mathbf{r}, \sigma\right) = \chi_S\{\hat{\mathbf{S}}_i\} \chi_\sigma \varphi(\mathbf{r}), \quad (3)$$

where $\chi\{\hat{\mathbf{S}}_i\}$ is the wave function of spins and χ_σ is the corresponding spin part for the carrier, whose spatial wave function is $\varphi(\mathbf{r})$. Using such wave function, one can average equation (1) with $\chi_S\{\hat{\mathbf{S}}_i\}$ and χ_σ and obtain

$$\mathcal{H}_e \varphi(\mathbf{r}) = \mathcal{H}_1 \varphi(\mathbf{r}) + \frac{1}{2} \left[g^* \mu_B \mathbf{H}_a + \frac{\alpha}{g \mu_B} \mathbf{M}(\mathbf{r}) \right] \cdot \boldsymbol{\gamma} \varphi(\mathbf{r}), \quad (4)$$

where $\mathbf{M}(\mathbf{r}) \equiv \langle \chi_S | \hat{\mathbf{S}} | \chi_S \rangle \times g \mu_B N_0$ is the local magnetization per unit volume; $N_0 = n_0/v_0$ is number of atoms per unit volume containing fraction x of magnetic atoms, $\alpha \equiv J_c v_0/n_0$ is the effective exchange constant, and $\boldsymbol{\gamma} = \sum_{\sigma, \sigma'} \langle \chi_\sigma | \boldsymbol{\sigma}_{\sigma\sigma'} | \chi_{\sigma'} \rangle$ is the polarization of the carrier spin. Consequently, we average now equation (4) and redefine \mathcal{H}_e in the following manner:

$$\mathcal{H}_C \equiv \langle \varphi | \mathcal{H}_1 | \varphi \rangle + \frac{1}{2} \boldsymbol{\gamma} \cdot \boldsymbol{\Delta}[\mathbf{M}; \varphi] \equiv \mathcal{H}_1 + \frac{1}{2} \boldsymbol{\gamma} \cdot \boldsymbol{\Delta}[\mathbf{M}, \varphi]. \quad (5)$$

In the preceding expression, the first term is the expectation value of the electron Hamiltonian \mathcal{H}_1 and the quantity

$$\Delta[\mathbf{M}; \varphi] \equiv \Delta_0 + \int d^3r [\mathbf{M}(\mathbf{r}) - \mathbf{M}_0] |\varphi(\mathbf{r})|^2, \quad (6)$$

is the resultant splitting of the donor state, with

$$\Delta_0 \equiv g^* \mu_B \mathbf{H}_a + \frac{\alpha}{g \mu_B} \mathbf{M}_0, \quad (7)$$

playing the role of the homogeneous part of the spin splitting for the electron [11], whereas \mathbf{M}_0 is the static part of the magnetization, i.e. the magnetization corresponding to the cation volume due to the average spins polarization. Note, that direction of Δ_0 defines a convenient quantization axis due to colinearity of \mathbf{H}_a and \mathbf{M}_0 .

The procedure of averaging equation (5), with respect to the fluctuating part of $\mathbf{M}(\mathbf{r})$, is as follows. We introduce the G–L functional for the spins, here taken with the quartic term

$$\mathcal{H}_S[\mathbf{M}] = \int \left\{ \frac{1}{2} \mu \mathbf{M}^2(\mathbf{r}) + \frac{1}{2} \xi^2 [\nabla \cdot \mathbf{M}(\mathbf{r})]^2 + \frac{1}{4} \lambda [\mathbf{M}^2(\mathbf{r})]^2 - \mathbf{H}_a \cdot \mathbf{M}(\mathbf{r}) \right\} d^3r, \quad (8)$$

where μ , ξ , and λ are the model parameters of the functional (see appendix A for its derivation from the Heisenberg model), μ is the inverse static magnetic susceptibility, ξ determines the characteristic (correlation) length, and the term $\sim \lambda$ introduces a quartic contribution to the system properties. Because we would like to analyze the role of thermodynamic fluctuations of magnetization on the BMP state in the vicinity of the magnetic phase transition, we consider both the longitudinal $\eta_{\parallel}(\mathbf{r})$ and the transverse, $\eta_{\perp}(\mathbf{r})$ fluctuations, with $\boldsymbol{\eta}(\mathbf{r}) \equiv \eta_{\parallel}(\mathbf{r}) + \boldsymbol{\eta}_{\perp}(\mathbf{r})$ and measured with respect to the static equilibrium magnetization \mathbf{M}_0 , i.e., $\mathbf{M}(\mathbf{r}) = \mathbf{M}_0 + \boldsymbol{\eta}(\mathbf{r})$. The corresponding contributions from $\mathbf{M}^2(\mathbf{r})$ are as follows:

$$\mathbf{M}^2(\mathbf{r}) = \mathbf{M}_0^2 + 2\boldsymbol{\eta}_{\parallel}(\mathbf{r}) \cdot \mathbf{M}_0 + \eta_{\parallel}^2(\mathbf{r}) + \boldsymbol{\eta}_{\perp}^2(\mathbf{r}), \quad (9)$$

and to the quartic term

$$[\mathbf{M}^2(\mathbf{r})]^2 = M_0^4 + 4\boldsymbol{\eta}_{\parallel}(\mathbf{r}) \cdot \mathbf{M}_0 M_0^2 + 6\eta_{\parallel}^2(\mathbf{r}) M_0^2 + 2\boldsymbol{\eta}_{\perp}^2(\mathbf{r}) M_0^2 + o(\mathbf{M}_0 \boldsymbol{\eta}^3, \boldsymbol{\eta}^4). \quad (10)$$

In other words, we consider the quartic contribution to $\mathbf{M}(\mathbf{r})$, but retain only the quadratic (Gaussian) fluctuations around this (non-zero) static value. The feature will lead to a spontaneous magnetic overall polarization within the polaron volume, even well above bulk T_c . Therefore, even in an isotropic solid, the appearance of $\mathbf{M}_0 \neq 0$ breaks the spin rotational symmetry and introduces a spontaneous polarization of the system. Substituting these expressions into \mathcal{H}_S give us the following explicit quadratic contributions:

$$\begin{aligned} \mathcal{H}_S[\mathbf{M}; \mu, \lambda] &= \mathcal{H}_S[\mathbf{M}_0; \mu, \lambda] + \mathcal{H}_S[\boldsymbol{\eta}; \mu, \lambda] \\ &\equiv \mathcal{H}_S[\mathbf{M}_0] + \int d^3r \left\{ \left(\mu + 3\lambda \mathbf{M}_0^2 \right) \frac{\eta_{\parallel}^2(\mathbf{r})}{2} + \frac{\xi^2}{2} [\nabla \cdot \boldsymbol{\eta}_{\parallel}(\mathbf{r})]^2 \right\} \\ &\quad + \int d^3r \left\{ \left(\mu + \lambda \mathbf{M}_0^2 \right) \frac{\boldsymbol{\eta}_{\perp}^2(\mathbf{r})}{2} + \frac{\xi^2}{2} [\nabla \cdot \boldsymbol{\eta}_{\perp}(\mathbf{r})]^2 \right\}, \end{aligned} \quad (11)$$

where the second and the third lines define \mathcal{H}_S and the contribution from $\nabla \cdot \mathbf{M}_0$ to $\mathcal{H}_S[\mathbf{M}_0]$ is zero. In effect, we have a full G–L functional to the fourth-order (the first term) and the Gaussian fluctuation contributions around an essentially mean-field state.

2.2. Spin splitting distribution

Next, we explore the use of the important simplification by assuming that $o(\mathbf{M}_0\eta^3, \eta^4) = 0$. Thus, we effectively account for only the quadratic (Gaussian) contribution to the magnetization fluctuations appearing around the resultant static value. Within this approximation, the following relation holds:

$$H_S[\eta; \mu, \lambda] = H_S[\eta; \bar{\mu}], \quad (12)$$

where

$$\bar{\mu}_i \equiv \begin{cases} \mu + 3\lambda\mathbf{M}_0^2 & \text{for } i = 3 \text{ (}\parallel\text{)} \\ \mu + \lambda\mathbf{M}_0^2 & \text{for } i = 1, 2 \text{ (}\perp\text{)} \end{cases}. \quad (13)$$

In other words, the contribution $\sim \lambda$ in the fluctuation part has been absorbed into the Gaussian part. This amounts to saying that the thermodynamics related to $\mathcal{H}_S[\eta; \mu, \lambda]$ can be determined directly from the well-known solution of the anisotropic Gaussian model, as carried out in [11]. To obtain the renormalized by fluctuations Hamiltonian for the donor electron, we follow that reference and define next the probability distribution of the magnetization fluctuations within electron in state $\varphi(\mathbf{r})$:

$$P[\eta(\mathbf{r}), \varphi(\mathbf{r})] \equiv \frac{\exp\{-\beta\Delta F[\eta(\mathbf{r}), \varphi(\mathbf{r})]\}}{\int D\eta(\mathbf{r}) \exp\{-\beta\Delta F[\eta(\mathbf{r}), \varphi(\mathbf{r})]\}}, \quad (14)$$

where $D\eta(\mathbf{r})$ symbolizes the functional integration over all possible space profiles of $\eta(\mathbf{r})$. Then the probability distribution of electron energies $P(E_R)$ is given by

$$\begin{aligned} P(E_R) &= C \sum_{\gamma=\pm 1} \int D\eta(\mathbf{r}) P[\eta(\mathbf{r})] \exp[-\beta(\mathcal{H}_C)] \\ &= 2C \exp\left[-\frac{\mathcal{H}_1}{k_B T}\right] \int D\eta(\mathbf{r}) \cosh\{\beta\Delta[\eta(\mathbf{r})]\} \exp\left[-\frac{\mathcal{H}_S}{k_B T}\right], \end{aligned} \quad (15)$$

where $C^{-1} \equiv \int D\eta(\mathbf{r}) \exp\{-\beta\mathcal{H}_S[\eta(\mathbf{r})]\}$. Note that we may use the preceding equation to define the effective renormalized Hamiltonian of the BMP in the following manner:

$$H_{\text{eff}} \equiv -k_B T \ln P(E_R). \quad (16)$$

The probability distribution of electron energies $P(E_R)$ is difficult to calculate. A significantly simpler task is to calculate the probability distribution $P(\Delta)$ of the spin splitting Δ , which is obtained by the appropriate change of variables, namely

$$P(\Delta) = \int P[\eta(\mathbf{r})] \exp\{-\beta\mathcal{H}_C\} \delta\{\Delta - \Delta[\eta(\mathbf{r})]\} D\eta(\mathbf{r}). \quad (17)$$

The meaning of the transformation is explained in [11] and its execution provides

$$P(\Delta) = 2C \exp\left(-\frac{\mathcal{H}_1}{k_B T}\right) \cosh\left(\frac{\Delta}{2k_B T}\right) Z[\Delta], \quad (18)$$

where

$$Z[\mathbf{\Delta}] = \int_{-\infty}^{\infty} D\boldsymbol{\eta}(\mathbf{r}) \exp \left(-\beta \int \left\{ \left[\bar{\mu}_{\parallel} \frac{\boldsymbol{\eta}_{\parallel}^2(\mathbf{r})}{2} + \frac{\xi^2}{2} [\nabla \cdot \boldsymbol{\eta}_{\parallel}(\mathbf{r})]^2 \right] + \left[\bar{\mu}_{\perp} \frac{\boldsymbol{\eta}_{\perp}^2(\mathbf{r})}{2} + \frac{\xi^2}{2} (\nabla \cdot \boldsymbol{\eta}_{\perp}(\mathbf{r}))^2 \right] \right\} \delta \{ \mathbf{\Delta} - \mathbf{\Delta}[\boldsymbol{\eta}(\mathbf{r})] \} d^3r \right). \quad (19)$$

To calculate the partition function $Z[\mathbf{\Delta}]$, one considers the fact that within our approximation the presence of equilibrium magnetization \mathbf{M}_0 influences $Z[\mathbf{\Delta}]$ by modifying the corresponding contribution $\mu \rightarrow \bar{\mu}$. Finally, performing analogous calculations as in [11], the partition function $Z[\mathbf{\Delta}]$ can be expressed as follows:

$$Z[\mathbf{\Delta}] = \prod_{i=1,2,3} \exp \left[-\frac{(\Delta_i - \Delta_{0i})^2}{8\epsilon_{pi} k_B T} \right], \quad (20)$$

where

$$\epsilon_{pi} \equiv |\varphi(\mathbf{r})|^2 \diamond_i |\varphi(\mathbf{r}')|^2 \left(\frac{\alpha}{g\mu_B} \right)^2 \quad (21)$$

and the operator \diamond_i is defined as

$$A_i(\mathbf{r}) \diamond_i B(\mathbf{r}') \equiv \frac{1}{4} \int \int A_i(\mathbf{r}) Q_i(\mathbf{r}, \mathbf{r}') B(\mathbf{r}') d^3r d^3r', \quad (22)$$

with the propagator $Q_i(\mathbf{r}, \mathbf{r}')$ explicitly given by the Ornstein–Zernike correlation function

$$Q_i(\mathbf{r}, \mathbf{r}') \equiv \int \frac{e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}}{\bar{\mu}_i + k^2 \xi^2} \frac{d^3k}{(2\pi)^3} = \frac{1}{4\pi \xi^2 |\mathbf{r} - \mathbf{r}'|} e^{-\frac{\sqrt{\bar{\mu}_i}}{\xi} |\mathbf{r} - \mathbf{r}'|}. \quad (23)$$

In expression (20), important parameters of the present approach appear, namely ϵ_{pi} , with $i = 1, 2$, and 3 . These quantities, for the case with $\lambda = 0$, reduce to ϵ_p of DS theory. This is not surprising because the DS theory may be regarded as the Gaussian limiting case ($\lambda = 0$) of the present approach. Note also, that it may be energetically favorable for the BMP to create a spontaneous polarization $\mathbf{M}_0 \neq 0$ of the spins only within its effective volume πa^3 when $\lambda \neq 0$. We discuss this feature of our results in the next section.

2.3. Thermodynamic properties

The next step, in analogy to [11], is to define a contribution ΔF to the free energy of the system, introduced by the presence of the donor electron that had formed the BMP state. Here, ΔF is defined as the difference between the free energy when donor is present and the spin part when donor is absent, i.e.,

$$\Delta F[\eta(\mathbf{r}), \psi(\mathbf{r})] = -k_B T \ln \left[\text{Tr}_{\{\sigma^z\}} \int d^3\Delta \exp\left(-\frac{\mathcal{H}_C + \mathcal{H}_S}{k_B T}\right) \right] + k_B T \int d^3\Delta \exp\left(-\frac{\mathcal{H}_S}{k_B T}\right). \quad (24)$$

This quantity represents contribution of one BMP and originates solely due to thermodynamic magnetization fluctuations as contributions from $\mathcal{H}_S[M_0]$ cancel out. For the system consisting of N^0 non-interacting BMPs in volume V , the magnetic part of the free energy $F(M_0)$ may be written in the following form:

$$F(\mathbf{M}_0)/V \equiv n^0 \Delta F(\mathbf{M}_0) + \frac{1}{2} \mu \mathbf{M}_0^2 + \frac{1}{4} \lambda \mathbf{M}_0^4 - \mathbf{H}_a \cdot \mathbf{M}_0. \quad (25)$$

where \mathbf{M}_0 is the static magnetization density and n^0 is the BMPs concentration. In the preceding expression, the second term represents the magnetic free energy density of spins considered here in the simple Landau approximation. Above T_c , it represents demagnetization energy. It should be noted that, that in [39], an expression for ΔF using the Feynman path integral method has been used to consider the spin polaron formation. Therefore, considering a BMP as a trapped conduction electron on the hydrogenic-like center, one can look to [39] as a precursor work. It should be stressed that the dependence of ΔF on M_0 has not been studied thus far.

Before presenting numerical results, we consider here a simple case with the parameter $\xi \rightarrow 0$. In such a case, an analytical expression for ϵ_{pi} can be determined. Namely, we have:

$$Q_i(\mathbf{r}, \mathbf{r}') = \bar{\mu}_i^{-1} \delta(\mathbf{r} - \mathbf{r}'), \quad (26)$$

thus

$$\epsilon_{pi} = \frac{\bar{\alpha}^2}{4 \bar{\mu}_i}, \quad (27)$$

where the constant $\bar{\alpha}$ is defined by the following expression:

$$\bar{\alpha} \equiv \frac{\alpha}{g\mu_B} \sqrt{\int d^3r |\varphi(\mathbf{r})|^4}. \quad (28)$$

Finally, the partition function $Z[\Delta]$ corresponding to ΔF may be written as follows:

$$Z[\Delta] = \exp\left(-\left\{\frac{[\Delta \cos(\theta) - \Delta_0]^2}{8\epsilon_{p\parallel} k_B T} + \frac{\Delta^2 \sin^2(\theta)}{8\epsilon_{p\perp} k_B T}\right\}\right), \quad (29)$$

where θ is the angle between Δ and Δ_0 . From equation (27), one can see that ϵ_{pi} is inversely proportional to dressed $\bar{\mu}_i$, which in turn includes the contribution proportional to $\lambda \mathbf{M}_0^2$. Therefore, the quadratic contributions to the magnetization fluctuations, originating from the quartic-term contribution in the effective functional for spins, are important.

3. Numerical results and comparison with experiment

We apply our model to the recently published experimental data on epitaxial films of GdN with varying doping levels [26]. In this ferromagnetic semiconductor, Gd^{3+} ions have spin $S = 7/2$ due to the half-filled $4f$ shell, with a net magnetic moment of $7\mu_B$ per Gd^{3+} ion. The carrier states originate from either hybridized $5d-6s$ states due to Gd or shallow donor states created on the charged nitrogen vacancies. Experimentally, the Curie temperature $T_c = 37$ K for the undoped semiconductor [26] increases with increasing doping, e.g., for a sample with carrier concentration at room temperature $n^- = 3.3 \times 10^{20} \text{ cm}^{-3}$, we see a sharp increase to the value of $T_c = 70$ K. The characteristic feature of this magnetic-semiconductor thin epitaxial film is the double dome structure of various physical quantities plotted vs. temperature, which has been ascribed to the presence of BMPs [26].

First, we determine the values of material parameters entering the G–L functional for the host magnetic semiconductor, namely μ , ξ , and λ . The inverse magnetic susceptibility can be expanded in the power series of λ , namely [40]

$$\frac{\beta}{\chi} \equiv \mu + \frac{\lambda}{2} \int_0^\Lambda \frac{d^3q}{\xi^2 q^2 + \mu} + o(\lambda^2), \quad (30)$$

where Λ is the integration cutoff. For the case with $\xi = 0$ that we consider here, the integral is proportional to the volume of the reciprocal space, and thus is regarded as negligible. Therefore, in such a situation

$$\mu = \beta/\chi. \quad (31)$$

Next, we assume that the magnetic susceptibility obeys the Curie–Weiss law:

$$\chi = \frac{C_M}{T - T_c}, \quad (32)$$

with the molar Curie constant given by

$$C_M = \frac{1}{3k_B} (g\mu_B)^2 S(S+1) N_0. \quad (33)$$

In this manner, the two parameters T_c and λ are sufficient to determine the free energy due to the spins. Figure 1 exhibits a comparison of the calculated temperature dependence of M_0 with experimental data for two GdN thin films (taken from [26]). The values of the parameters are then: $T_c = 41$ and 55 K, with $\lambda = 0.93N_0^{-3}$ and $1.16N_0^{-3}$, corresponding to the room temperature carrier concentrations $n^- = 10^{18} \text{ cm}^{-3}$ (sample L) and $3.3 \times 10^{20} \text{ cm}^{-3}$ (sample M), respectively. Generally, one can see from figure 1 that the Landau approximation (solid lines) to the G–L Hamiltonian describes data at temperatures ranging from 10 to 40 K quite well. However, in the critical region, discrepancies are substantial and significantly larger for the sample with higher donor concentration. The deficiency of the Landau approximation is its insensitivity to the short-range ordering, which smears out the phase transition. To estimate the amplitude of this effect, we treated the external magnetic field as an adjustable parameter B' and verified that its value of $3 T$ can significantly improve the description of the data for the sample with lower donor concentration (dashed lines in figure 1). For the sample with the higher donor concentration, the same procedure fails, even with a higher value of the correction field $B' = 4$ T. Assuming now, that we can account for the contribution due to the short-range ordering by

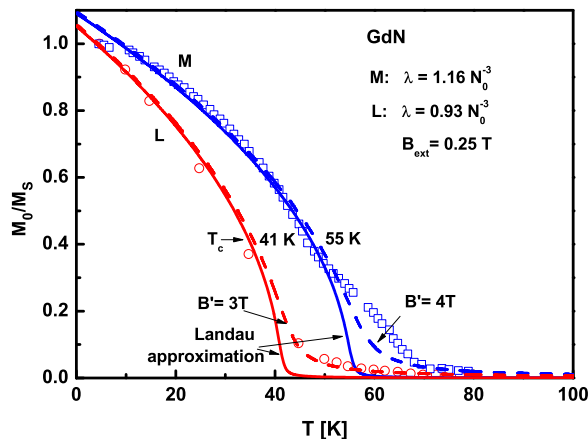


Figure 1. Comparison of normalized magnetization (solid lines) calculated within the Landau approximation, and without BMPs contribution, with the experimental data (open symbols) for two samples, labeled L and M of GdN vs. temperature. The dashed lines correspond to the Landau approximation corrected with an extra field (B') contribution emulating the short-range ordering. Data are taken from [26].

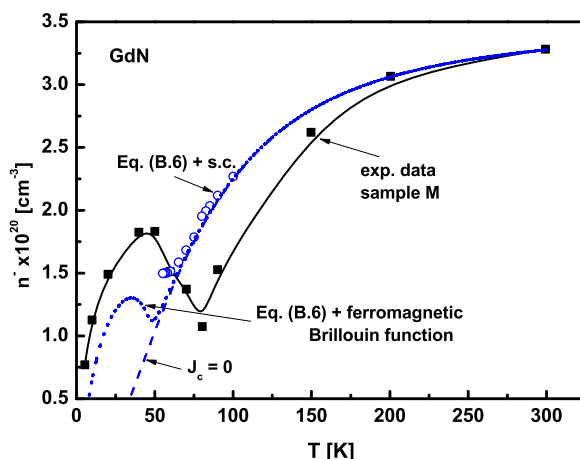


Figure 2. Comparison of the calculated (open symbols and dotted line) temperature dependence of the carrier concentration for sample M with experimental data (closed symbols) taken from [26].

introducing a correction field B' , which simply adds to the external magnetic field, we can account for the remaining contribution to the magnetization of the sample M as caused by the presence of BMPs. Thus, the presence of an extra field B' mimics the effect of a short-range order or other higher-order effects. It is rewarding that such a simple extra factor is sufficient to rationalize the data on a semi-quantitative level.

Having determined the values of the spin-functional parameters for the host magnetic semiconductor, we need to establish the values of parameters related to the impurity state. Most interesting for us is the neutral donor concentration $n^0 \equiv n_d - n^-$, where n_d is the total donor concentration, which enters the expression for $F(M_0)/V$. Its temperature dependence is crucial and is calculated in appendix B. In figure 2, we compared calculated (open symbols and dotted line) carrier concentration n^- for the sample M with experimental data (closed symbols and

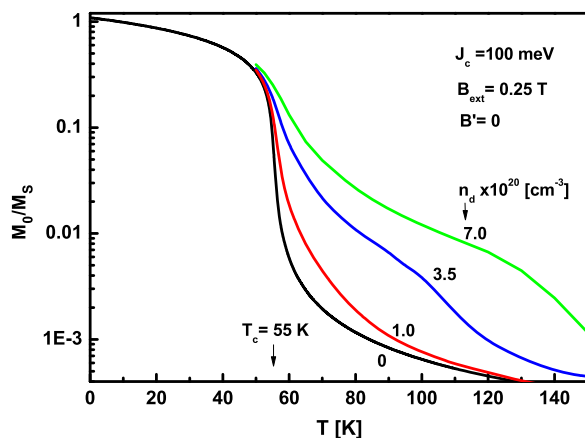


Figure 3. The calculated normalized magnetization as a function of temperature, with contribution due to BMPs included, for $T_c = 55$ K, $J_c = 100$ meV, and for the four selected values of the donor concentration n_d .

solid line) taken from [26]. The calculation of n^- has been carried out using (B.6) with two approaches describing M_0 namely, either minimizing the system free energy (open circles) or using the Brillouin function for ferromagnetic case (dotted line). It is apparent from figure 2 that the double-dome structure of $n^-(T)$ is caused by the exchange contribution to the donor energy, because for the situation with $J_c = 0$, we obtain a monotonic curve (dashed line). This composes the signature of the BMP in ferromagnetic semiconductors. Our present approach underestimates the contribution due to the s-f exchange.

Following [26], we assume that the effective mass $m^* = 0.15m_0$ and the static dielectric constant is $\epsilon = 4$, which leads to the effective donor Bohr radius $a_B \approx 1.4$ nm. Thus, there are 400 Gd^{3+} cations within the BMP radius in GdN. We can now calculate the system free energy originating from the presence of BMPs. Explicitly, it has the form

$$\begin{aligned}
 F(M_0)/V = & n^0 \left(\frac{\hbar^2}{2m^*a_B^2} - \frac{e^2}{\epsilon a_B} \right) + \left(\frac{1}{2}\mu M_0^2 + \frac{1}{4}\lambda M_0^4 - H_a M_0 \right) \\
 & - n^0 k_B T \ln \int \int \int \Delta^2 \sin(\theta) \left[\cosh\left(\frac{\Delta}{2k_B T}\right) - 1 \right] \\
 & \times \exp \left\{ - \left[\frac{(\Delta \cos(\theta) - \Delta_0)^2}{8\epsilon_{p\parallel} k_B T} + \frac{\Delta^2 \sin^2(\theta)}{8\epsilon_{p\perp} k_B T} \right] \right\} d\phi d\theta d\Delta. \quad (34)
 \end{aligned}$$

It should be stressed that n^0 depends not only on T but also on M_0 through the donor energy [see expressions (B.1) and (B.6)].

To study the magnetic properties of our model, we calculated magnetization varying both the total donor concentration n_d and the exchange integral J_c , which are included in a quantitative manner in figures 3 and 4, respectively. In figure 3, we show the temperature dependence of the equilibrium magnetization, i.e., the magnetization corresponding to the minima $F(M_0, T)$, calculated for $T_c = 55$ K and four values of $n_d = 0, 1, 3.5, \text{ and } 7 \times 10^{20} \text{ cm}^{-3}$. In figure 4,

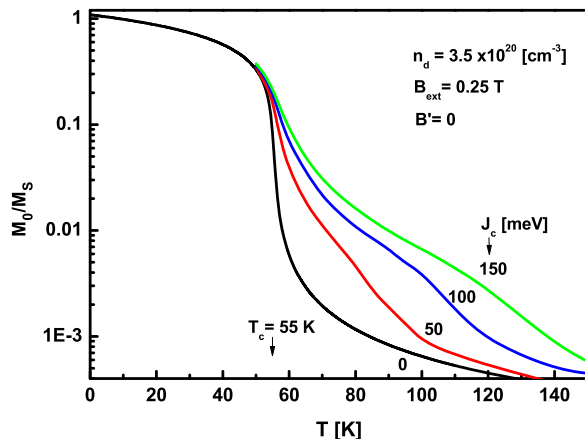


Figure 4. The same as in figure 3 but for the fixed donor concentration $n_d = 3.5 \times 10^{20} \text{cm}^{-3}$ and four selected values of J_c .

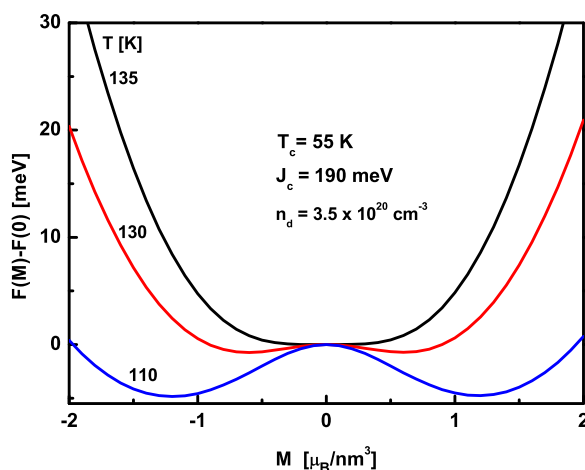


Figure 5. The free energy of BMP encompassing spins $S = 7/2$ as a function of static magnetization density for $T_C = 58 \text{ K}$ and $\bar{\alpha} = 2 \text{ T}$ calculated for the three indicated temperatures and $V = 5.5 \text{ nm}^3$. For comparison, the fully saturated magnetization due to the spins is $M_s = 224 \mu_B/\text{nm}^3$.

we also show the normalized magnetization but calculated for four values of $J_c = 0, 50, 100,$ and 150 meV .

The limit $J_c = 0, \Delta F \equiv 0$ reflects the situation without the BMP state. Note a striking agreement of the results presented in figure 3 with the experimental data for EuO of [25] (see figure 2 in [25]). The polaronic contribution above T_c is clearly visible for $J_c > 0$ in both figures and thus, our model also provides the double-dome feature for the free energy curve caused by the formation of BMPs. In figure 5, we plotted the calculated dependence F on M_0 for various temperatures. The Mexican hat shape signaling the onset of the magnetic order in the BMP starts developing below $T = 135 \text{ K}$. However, the magnitude of this effect is low for temperatures in that regime. Nevertheless, within the assumed value of the model parameters, the equilibrium magnetization density is small but clearly non-zero, even at 130 K . The evolution of the Mexican hat feature is in the last situation gradual and effectively, the polaron

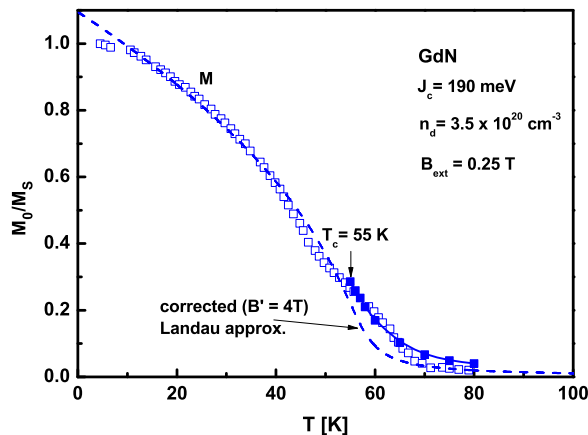


Figure 6. Comparison of calculated normalized magnetization with the BMPs and B' contributions included (closed symbols and solid line) with the experimental data (open symbols) for GdN vs. temperature. The dashed line corresponds to the calculated system magnetization when BMP is not formed ($J_c = 0$). Data are taken from [26].

effect destroys the notion of the critical temperature. This is one of the crucial features, by which the present approach differs from any other mean-field treatment. The assumed value of $J_c \simeq 190$ meV can be compared with that calculated for GdN [41], $J_c = 350$ meV, or that for EuO [1], $J_c = 110$ meV. Note that here, we take the donor radius a_B as unchanged due to the presence of spins, even though it changes slightly due to the s - f interaction [11–14].

In figure 6, we compared, in a quantitative manner, our theoretical results for $T_c = 55$ K and $J_c = 190$ meV to the experimental data reported in [26] for GdN. As can be seen, the overall agreement is very good. The high temperature magnetization is slightly overestimated by our model, but in the vicinity of T_c , the agreement is excellent even though we have put $\xi = 0$. This assumption may seem surprising initially. However, for $T > T_c$, the triggering field ordering the spins within the BMP is the local s - f exchange field. Hence, the intersite coupling seems less relevant. However, one should be aware that the Ruderman–Kittel–Kasuya–Yosida interaction between the spins is contained only implicitly via the parameter T_c .

Nonetheless, in spite of the simplicity of the developed model, i.e., that it neglects both the carrier-density dependence of spin–spin interactions, as well as the interactions between individual BMPs [20–23], its validity has been clearly demonstrated.

4. Conclusions and outlook

In this work, we have essentially extended the theory [11] valid for the single BMP in a paramagnetic DMS to the situation of a ferromagnetic semiconductor. This has been completed by including in the system effective Landau spin Hamiltonian the quartic term. A non-zero magnetization within the BMP cloud persists to temperatures well above T_c and is in agreement with the recent experimental data reported by Natali *et al* [26] for GdN, as well as with the previous theoretical investigations on other ferromagnetic semiconductors [10, 39].

The present continuous-medium approximation is effective because of two factors. First, the size of the BMP is relatively large (≈ 1.5 nm) and encompasses $N \approx 400$ Gd^{3+} spins of magnitude $S = 7/2$. Previously [15], it has been shown for the case with Gaussian fluctuations, that the spin

cloud composed of $N > 4$ spins of magnitude $S = 5/2$ is represented already rather well by continuous distribution of exchange field acting on the donor electron. Second, the spin magnitude $S = 7/2$ is the largest possible and makes the quantum aspects of fluctuations negligible. In general, the thermal behavior of the spin splitting $\Delta(T)$, demonstrates once more [42] the influence of the thermodynamic fluctuation on a quantum (donor in the present case) state of individual electron. However, inclusion of a number of polarons $n_d - n^-$ must be assumed, as well as an extra B' field, which is required to account quantitatively the data for small n_d .

One should note that, in this formulation, we have not tackled explicitly the most general case of non-Gaussian fluctuations starting from the effective Hamiltonian $\mathcal{H}_e + \mathcal{H}_S$, which is given by equation (5) and \mathcal{H}_S by equation (8). The splitting (6) plays the role of the inhomogeneous field acting on the spins. To tackle such a problem, a generalization of the standard renormalization group approach [40] would be required. Only then one can seriously analyze the strongly polarized BMP states for $T \ll T_c$ such as those that appear in EuO and related magnetic semiconductors [2–4], where the magnetic contribution to the BMP binding energy becomes predominant.

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Appendix A. Microscopic derivation of the G–L functional for spins with a brief overview

We briefly sketch the microscopic derivation of the Ginzburg–Landau functional for the spins and estimate the values of the parameters μ , λ , and ξ explicitly.

We start by decoupling the scalar product of the spins in a Hartree–Fock manner in a spatially inhomogeneous case:

$$\mathbf{S}_i \cdot \mathbf{S}_j \simeq \mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle + \langle \mathbf{S}_j \rangle \cdot \mathbf{S}_i - \langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle \cdot \mathbf{S}_j. \quad (\text{A.1})$$

Therefore, the Heisenberg spin–spin interaction takes the form:

$$\mathcal{H} = -\frac{1}{2} \sum'_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \simeq - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle - \frac{1}{2} \sum'_{ij} J_{ij} \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle. \quad (\text{A.2})$$

The free energy then takes the form:

$$F = -Nk_B T \ln \frac{\sinh \left[x_i \left(S + \frac{1}{2} \right) \right]}{\sinh \left(\frac{1}{2} x_i \right)} + \frac{1}{2} \sum_{i \neq j} J_{ij} \langle S_i^z \rangle \langle S_j^z \rangle, \quad (\text{A.3})$$

where

$$x_i \equiv \frac{\sum_{j(i)} J_{ij} \langle S_j^z \rangle + g\mu_B H_a}{k_B T}.$$

Formally, F is a functional of both H_a and magnetization M ; hence, it represents a generalization form of the free energy normally regarded as a function of state. This is why it is called Landau (or G–L) free energy. The first term is associated with the mean-field dynamics, whereas the second cancels out the double counting of interaction when taking the average over the spin degrees of freedom. Making a continuous-medium approximation for the second term, we obtain, for a cubic system

$$\frac{1}{2} \sum_{j(i)} J_{ij} \langle S_i^z \rangle \langle S_j^z \rangle \approx \frac{1}{2} J_0 \langle S^z(\mathbf{r}) \rangle^2 + \frac{1}{2} J_0 a_0^2 \langle S^z(\mathbf{r}) \rangle \nabla^2 \langle S^z(\mathbf{r}) \rangle \Big|_{\mathbf{r}=\mathbf{R}_i}, \quad (\text{A.4})$$

where $J_0 = J_z$, if we take only the interactions between z nearest neighbors, and a_0 is the lattice parameter. We assume additionally that, as we approach the phase-transition point, $T = T_c$, $\langle S^z(\mathbf{r}) \rangle \ll S$. Therefore, we may expand the hyperbolic function as

$$\sinh(ax) = ax + \frac{(ax)^3}{3!} + \frac{(ax)^5}{5!} + o(x^7). \quad (\text{A.5})$$

In effect,

$$\begin{aligned} \frac{\sinh\left[\left(S + \frac{1}{2}\right)x\right]}{\sinh\left(\frac{x}{2}\right)} &\approx (2S + 1) \frac{1 + \left(S + \frac{1}{2}\right)^2 \frac{x^2}{6} + \left(S + \frac{1}{4}\right)^4 \frac{x^4}{120}}{1 + \frac{x^2}{6} + \frac{x^4}{120}} + \dots \\ &\approx (2S + 1) \left[1 + \frac{1}{6} S(S + 1)x^2 + \frac{1}{360} \right. \\ &\quad \left. \times S(-1 + 2S + 6S^2 + 3S^3)x^4 + \dots \right]. \end{aligned} \quad (\text{A.6})$$

Hence, the free energy per site can be written (to second-order in x and with $H_a = 0$)

$$\begin{aligned} \frac{F}{N} &\simeq -k_B T \ln(2S + 1) - \frac{S(S + 1)}{6k_B T} \left[J_0 \langle S^z(\mathbf{r}) \rangle + J_0 a_0^2 \nabla^2 \langle S^z(\mathbf{r}) \rangle \Big|_{\mathbf{r}=\mathbf{R}_i} \right]^2 \\ &\quad + \frac{1}{2} J_0 \langle S^z \rangle^2 + \frac{1}{2} J_0 a_0^2 \langle S^z(\mathbf{r}) \rangle \nabla^2 \langle S^z(\mathbf{r}) \rangle \Big|_{\mathbf{r}=\mathbf{r}_i} + o(x^4). \end{aligned} \quad (\text{A.7})$$

The first term is the free energy F_0/N of one non-interacting spin. Regrouping the terms, we obtain

$$\frac{F}{N} \simeq \frac{F_0}{N} + \frac{J_0}{2} \left(1 - \frac{T_c}{T} \right) \langle S^z \rangle^2 - J_0 \left(\frac{T_c}{T} - \frac{1}{2} \right) a_0^2 \langle S^z \rangle \nabla^2 \langle S^z \rangle + o(x^4). \quad (\text{A.8})$$

Strictly speaking, in the continuous-medium approximation, F/N represents a free energy density. Therefore, the total free energy functional in a space of d dimensions is

$$F = \int \frac{d^d x}{v_0} \left[\frac{F_0}{N} + \frac{J_0}{2} \left(1 - \frac{T_c}{T} \right) \langle S^z \rangle^2 - J_0 \left(\frac{T_c}{T} - \frac{1}{2} \right) a_0^2 \langle S^z \rangle \nabla^2 \langle S^z \rangle + o(x^4) \right], \quad (\text{A.9})$$

where v_0 is the volume per spin (in the simple cubic case $v_0 = a_0^3$). Integrating the third term by parts and neglecting the surface term (not always feasible), we obtain

$$F = F_0 + \int \frac{d^d x}{\Omega_0} \left\{ -\frac{J_0}{2} \left(\frac{T_c - T}{T} \right) \langle S^z \rangle^2 + J_0 a_0^2 \left(\frac{T_c}{T} - \frac{1}{2} \right) \left[\nabla \langle S^z(\mathbf{r}) \rangle \right]^2 + o(x^4) \right\}. \quad (\text{A.10})$$

We will now concentrate on the analysis of the ferromagnetic phase transition in this Landau approach. For this purpose we must first introduce the higher-order term $\sim x^4$ in the expansion (A.6) that we have thus far neglected and we also generalize the definition of x to include the applied magnetic field H_a . We set the effective field as $H = (g\mu_B)^{-1} J_0 \bar{S}^z + H_a$ and then $x = \beta(g\mu_B H_a + J_0 \bar{S}^z)$. The lowest-order term in the expansion (A.6) will be truncated at the term linear in H_a ; thus $x^2 \approx \beta^2 (2g\mu_B J_0 \bar{S}^z H_a + J_0^2 \bar{S}^{z^2})$, where the contribution $2\beta^2 g\mu_B J_0 \bar{S}^z H_a$ must now be added to equation (A.6). Additionally, we consider the fourth-order contribution in $x = \beta J_0 \bar{S}^z$. We then follow all of the steps that lead from equation (A.6) to equation (A.9) to also obtain the quartic term in an explicit form:

$$\begin{aligned} \frac{F}{N} = \frac{F_0}{N} - \frac{3k_B(T_c - T)}{2S(S+1)} \bar{S}^{z^2} + \frac{1}{2} J_0 a_0^2 (\nabla \bar{S}^z)^2 - \frac{1}{3} \frac{S(S+1)}{k_B T} g\mu_B J_0 \bar{S}^z H_a \\ + \frac{\beta^3}{72} \left[S^2(S+1)^2 - \frac{S}{5} (-1 + 2S + 6S^2 + 3S^3) \right] (J_0 \bar{S}^z)^4. \end{aligned} \quad (\text{A.11})$$

We next replace the coefficient before \bar{S}^{z^2} in the first term with $\frac{\mu}{2}$, the coefficient before \bar{S}^{z^4} with $\frac{\lambda}{4}$, the coefficient before $(\nabla \bar{S}^z)^2$ with C , and set $\frac{S(S+1)J_0}{3k_B T} = \frac{T_c}{T} \approx 1$. This latter approximation is routinely used as the explicit form of the starting functional (8) for the temperature range near the phase transition. Finally, we obtain

$$\frac{F}{N} = \frac{F_0}{N} - \frac{\mu}{2} (T_c - T) \bar{S}^{z^2} + \frac{\lambda}{4} \bar{S}^{z^4} + C (\nabla \bar{S}^z)^2 - g\mu_B \bar{S}^z H_a + o(x^6), \quad (\text{A.12})$$

where $\mu = \frac{3k_B}{S(S+1)} (T_c - T)$, $\lambda = \frac{(k_B T_c)^3 J_0^4}{18} [\dots]$, and $C = \frac{1}{2} J_0 a_0^2$ are positive numbers. We see that, in general, the coefficients depend weakly on T ; this is why it has been neglected in the text by replacing T with T_c .

Consider first the zero-field spatially homogeneous solution, i.e., with when $\nabla \bar{S}^z \equiv 0$. This condition $\partial F / \partial \bar{S}^z = 0$ yields

$$\bar{S}^z = 0 \quad \text{or} \quad \bar{S}^z = \left[\frac{A}{B} (T_c - T) \right]^{\frac{1}{2}}. \quad (\text{A.13})$$

The first non-magnetic solution leads to the free energy $F = F_0$, whereas the second (magnetic) solution, which exists only for $T < T_c$ yields

$$\frac{F}{N} = \frac{F_0}{N} - \frac{\mu^2}{4\lambda}. \quad (\text{A.14})$$

Thus, the magnetic solution is the physically stable for $T \leq T_c$.

One can introduce a simple scaling of the free energy in the general case $\langle S^z \rangle = \langle S^z(\mathbf{r}) \rangle$ by defining the relative order parameter as

$$\eta(\mathbf{r}) = \frac{\bar{S}^z(\mathbf{r})}{\bar{S}^z} \equiv \frac{\bar{S}^z(\mathbf{r})}{\sqrt{\frac{\mu_0}{\lambda} (T_c - T)}}, \quad (\text{A.15})$$

and introducing effective length $x \Rightarrow \frac{x}{\xi}$, where the characteristic distance (the correlation length) is given by

$$\xi \equiv \left[\frac{2\lambda C}{\mu_0(T_c - T)} \right]^{-\frac{1}{2}}. \quad (\text{A.16})$$

Under these conditions, the free energy expression requires an integration over all the space we obtain for $T \leq T_c$

$$F = -Nk_B T \ln(2S + 1) - \frac{\mu_0^2}{4\lambda} (T_c - T)^2 \int \frac{d^d x}{\Omega_0} \left\{ 2\eta^2(x) - \eta^4(x) - [\nabla\eta(x)]^2 \right\}. \quad (\text{A.17})$$

The integration gives rise to a number. This form provides a universal dependence on temperature

$$F = F_0 - \alpha' \left(1 - \frac{T}{T_c} \right)^2. \quad (\text{A.18})$$

The coefficients μ and λ contain the total exchange interaction strength (in general $J_0 = \sum_{j(i)} J_{ij}$) and the value of T_c . Therefore, it is convenient to treat them, more or less, as free parameters, as we did in the main text. They can serve as a good estimate of the spin–spin exchange integral only when the interaction between the nearest neighbors is dominant.

Appendix B. Temperature dependence of the electron concentration

Here, we calculate the occupied donor concentration. Decreasing temperature number of localized carriers increases according to the Fermi–Dirac statistic and is determined mainly by the donor activation energy, which now contains the polaronic contributions and the number of donors n_d . The donor activation energy depends on the position of the donor level E_d relative to the position of the bottom of the conduction band ε_c , as well as the exchange contribution. Following [26] and [43], we also assume that each nitrogen vacancy binds two electrons in a singlet state, with a third electron in the $2s$ state. Explicitly, we take

$$\varepsilon_d = \frac{1}{4}E_d - \frac{\alpha}{2}\langle S^z \rangle. \quad (\text{B.1})$$

Next, the average number of ionized donors n_d^+ is given by [44]:

$$n_d^+ = \frac{n_d}{1 + 2e^{(\mu - \varepsilon_d)/k_B T}}, \quad (\text{B.2})$$

where μ is the chemical potential. Whereas, the density of electrons n^- :

$$n^- = \frac{N}{e^{(\varepsilon_c - \mu)/k_B T} + 1}, \quad (\text{B.3})$$

where N is defined by the following integral:

$$N \equiv \int_{\varepsilon_c}^{\infty} \rho(\varepsilon) e^{(\varepsilon - \varepsilon_c)/k_B T} d\varepsilon, \quad (\text{B.4})$$

and the density of states in the conduction band $\rho(\varepsilon)$ is taken from the effective mass theory, namely

$$\rho(\varepsilon) \equiv \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon - \varepsilon_c}. \quad (\text{B.5})$$

The neutrality condition $n_d^+ = n^-$ allows us to calculate μ and then n^- from equation (B.3). Finally, we obtained the following expression for the electron concentration:

$$n^- = \frac{N}{\frac{\sqrt{N^2 - 2n_d N + 8Nn_d e^{-\frac{\varepsilon_d}{k_B T}} + n_d^2} + N - n_d}{2n_d} + 1}. \quad (\text{B.6})$$

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