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

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(Received 23 September 1982)

We consider the magnetic field and temperature dependences of the spin splitting for an electron localized on a shallow donor, taking into account the *s-d* coupling with the surrounding magnetic ions. We calculate the probability distribution of the spin splitting Δ with the thermodynamic fluctuations of magnetization included. They are responsible for persistence of the spin splitting at ambient temperature in the absence of the field. The probability distribution of the spin splitting is the main factor determining the energy and the shape of the optical transition line between the spin-split states. We compare our results with recent experimental results on spin-flip Raman scattering in $Cd_{1-x}Mn_xSe$. Our theory provides a satisfactory quantitative description of the donor electron accompanied by a nonuniform cloud of magnetization in that material.

I. INTRODUCTION

The properties of a shallow donor electron accompanied by a nonuniform spin polarization of localized $3d$ or $4f$ electrons (hereafter simply called the spins) have been studied intensively during the last decade.[1-5] Since the *s-d* (*s-f*) coupling of spins to carriers is important in this case, a detailed analysis of the influence of this coupling on the binding energy and on the localization of the wave function of the impurity electron should be given.[3-5] The resultant bound state for which both electrostatic and magnetic (*s-d* coupling) energies are important is called a bound magnetic polaron (BMP).[1,2] The importance of the concept of the BMP shows itself when analyzing the strong transport anomalies of doped ferromagnetic semiconductors EuO and EuS, particularly near the Curie temperature and in the paramagnetic regime.[1,2,6,7] The polaronic effects are also important when considering the influence of the *s-d* coupling on spin splitting of extended (carrier) states in these semiconductors.[8]

In this paper our interest is concentrated on dilute magnetic semiconductors.[9] The purpose of this work is to help in understanding the optical properties[10-12] of the system $Cd_{1-x}Mn_xSe$, with x well below the percolation limit ($x_c \simeq 0.2$) for the onset of the magnetic order of Mn^{2+} ions. However, unlike the previous theoretical treatments of the bound paramagnetic polaron,[1-5,10,13] we take into account the effect of thermodynamic fluctuations of magnetization on the binding energy of the electron localized on the donor.[14] The new feature of our considerations is based on the observation that a degree of spin alignment around the donor may be caused not only by the molecular field produced by the impurity electron but also by the thermodynamic fluctuation of magnetization. The influence of the latter factor can be relatively large even beyond the critical region because of the finite size of the system under consideration. Additionally, we show how a spurious phase transition to BMP state, obtained within the mean-field approximation,[1,7] can be removed when the thermodynamic fluctuations are treated more carefully.

The structure of this paper is as follows. We start with the equation of motion for the donor electron coupled through the *s-d* coupling with dilute Heisenberg spins and define the spin splitting (Sec. II). Next, in Sec. III we derive the Ginzburg-Landau functional using the rotationally invariant form of the molecular-field approximation (Sec. III A). This functional helps us to derive the effective Hamiltonian containing the spin splitting $|\vec{\Delta}|$ as a variable and the effective Bohr radius a as a variational parameter. The effective Hamiltonian is averaged out over all space profiles $\{\vec{M}(\vec{r})\}$ of the local magnetization of the spins giving rise to a specific value of $|\vec{\Delta}|$. The nonvanishing value of $\vec{M}(\vec{r})$ when the magnetic field is absent comes from both the *s-d*

coupling and the thermodynamic fluctuations. The latter factor is a decisive one at nonzero temperature since we do not expect any spontaneous magnetic order at $T \neq 0$ for the dilute system interacting with the donor electron within a finite volume ($\sim a^3$) only. The effective Hamiltonian gives the probability distribution $P(|\vec{\Delta}|)$ of the spin splitting, in accordance with the fact that the probability for a given fluctuation to appear is given by the Boltzmann distribution with the energy being the amount of the free energy needed to create the fluctuation. This probability distribution determines both the thermodynamics (Sec. IV) and the shape of the line in optical transition (Sec. V is where the detailed comparison with the experiment is given). Section VI contains discussion and a short summary of our results. Finally, the Appendixes A–D give some details of our calculations as well as some of the material parameters of the systems for which the numerical calculations were performed (cf. Appendix D).

II. EQUATION OF MOTION AND THE SPIN SPLITTING

We assume that we have an electron on a shallow donor placed below the bottom edge of the conduction band, which has its minimum for wave vector $\vec{k}=0$. The Hamiltonian of this electron can be written as

$$H = H_B + H_C + H_M \ , \tag{2.1}$$

where H_B is the band energy near the bottom of the conduction band, $H_C = -e^2/\kappa r$ is the Coulomb attraction energy to the donor, and

$$H_M = -J_C \sum_i \vec{S}_i \cdot \vec{s}_i + g^* \mu_B \vec{H} \cdot \sum_i \vec{s}_i$$

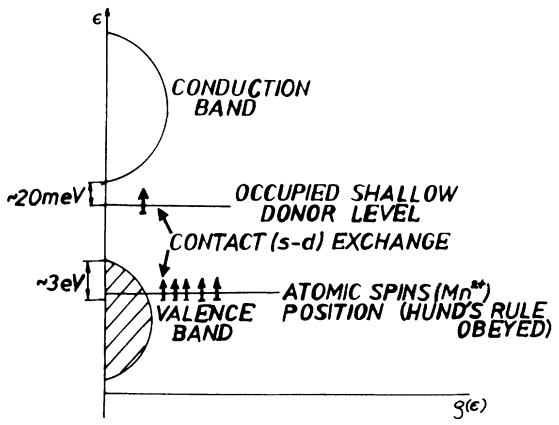

FIG. 1. Schematic representation of the situation considered in this paper. We disregard the thermal activation of the donor electron.

is the magnetic part containing both the *s-d* interaction with localized moments $\{\vec{S}_i\}$ (called briefly hereafter the spins) and the Zeeman term. The situation is schematically represented in Fig. 1. We assume also that the spins are placed on a regular lattice and dilute with nonmagnetic ions so that they can be treated as a paramagnetic subsystem with localized magnetic moments.

The wave function of the electron can be written as[15]

$$|\Psi\rangle = \sum_{n,\sigma} \varphi_{n\sigma} a^\dagger_{n\sigma} |0\rangle \ , \tag{2.2}$$

where $\varphi_{n\sigma}$ is the amplitude of electron on site $\vec{R}_n$, with spin σ, $a^\dagger_{n\sigma}$ is the creation operator of electron on this site and $|0\rangle$ means the vacuum state, with no electron present. Here we consider a single electron on donor. The wave function leads to the following Schrödinger equation for the electron[15]:

$$i\hbar \partial_t \varphi_{n\sigma} - \sum_{m(n)} t_{mn} \varphi_{m\sigma} - \left[\epsilon_C^0 - \frac{e^2}{\kappa |R_n|} \right] \varphi_{n\sigma} - \tfrac{1}{2} g^* \mu_B \vec{H} \cdot \sum_{\sigma'} (\vec{\tau})_{\sigma\sigma'} \varphi_{n\sigma'} + \tfrac{1}{2} J_C \sum_{\sigma'} (\vec{S}_n \cdot \vec{\tau})_{\sigma\sigma'} \varphi_{n\sigma'} = 0 \ . \tag{2.3}$$

This is the Schrödinger equation in real space, so t_{mn} is the overlap integral between the Wannier states $\Phi_C(\vec{r}-\vec{R}_m)$ and $\Phi_C(\vec{r}-\vec{R}_n)$ for the conduction band, ϵ_C^0 is the position of the bottom edge of the conduction band, κ is the static dielectric constant of the medium, J_C is the exchange constant of the contact Fermi interaction between localized spins $\{\vec{S}_i\}$ and the donor electron, and $\vec{\tau}=(\tau_x,\tau_y,\tau_z)$ are the Pauli matrices. In what follows we will consider a large-polaron case. Then, using the continuous medium and effective-mass approximations, we get[15]

$$i\hbar \partial_t \varphi_\sigma(\vec{r},t) = \frac{-\hbar^2}{2m^*} \nabla^2 \varphi_\sigma(\vec{r},t) - \frac{e^2}{\kappa r} \varphi_\sigma(\vec{r},t) + \tfrac{1}{2} g^* \mu_B \vec{H} \cdot \sum_{\sigma'} (\tau)_{\sigma\sigma'} \varphi_{\sigma'}(\vec{r},t) - \tfrac{1}{2} J_C \sum_{\sigma'} (\hat{\vec{S}}(\vec{r},t) \cdot \vec{\tau})_{\sigma\sigma'} \varphi_{\sigma'}(\vec{r},t) \ . \tag{2.4}$$

We make one further approximation. Namely, we replace the spin field $\hat{\vec{S}}(\vec{r},t)$ by its quantum-mechanical average. This is the so-called molecular-field approximation and it means we neglect the spin-flip processes, i.e, the processes of

the exchange of unit spin between the subsystem of the spins and the donor electron. Also, we assume that the time evolution of the spin subsystem in the large-polaron case considered is slow enough so that we can regard it as a static subsystem (stationary states considered only). These facts are in agreement with the observation that the donor electron "sees" a large cloud of spins which therefore can be regarded as an effective classical spin $S_{\text{eff}} \to \infty$. So, both the spin-flip processes and the time evolution of the individual spin out of the cloud are regarded here as irrelevant to the problem, and therefore the thermalization process of the donor electron is assumed to take place for every configuration of the cloud.

Thus we seek a solution in the form

$$\varphi_\sigma(\vec{r},t)=\exp\left[-\frac{iH_e t}{\hbar}\right]\varphi_\sigma(\vec{r}) , \tag{2.5}$$

where the electronic Hamiltonian H_e of our system is

$$H_e=-\frac{\hbar^2}{2m^*}\nabla^2-\frac{e^2}{\kappa r}+\tfrac{1}{2}\alpha\vec{\mathrm{M}}(\vec{r})\cdot\vec{\tau} + \tfrac{1}{2}g^*\mu_B\vec{\mathrm{H}}\cdot\vec{\tau} , \tag{2.6}$$

with local magnetization

$$\vec{\mathrm{M}}(\vec{r})=-g\mu_B\frac{n_0\langle\hat{\vec{\mathrm{S}}}(r)\rangle}{V_0} , \tag{2.7}$$

and

$$\alpha=\frac{J_C V_0}{n_0} , \tag{2.8}$$

where V_0 is the volume of the elementary cell containing n_0 cations, g and g^* are the Landé factors for the spins and the donor electron, respectively.

Next, to make the problem tractable we decompose wave function $\varphi_\sigma(\vec{r})$ into space and spin parts, i.e., $\varphi_\sigma(\vec{r})=\varphi(\vec{r})\alpha_\sigma$, and define the spin Hamiltonian H_C for the donor electron as Hamiltonian (2.6) averaged over space variables, i.e.,

$$H_C=\int d^3r\,\varphi^*(\vec{r})H_e\varphi(\vec{r}) . \tag{2.9}$$

We are considering a single donor in a semiconductor with N_D such impurities in unit volume, each occupied by an electron. What is of interest to us, therefore, is a range of concentrations below the one determining the Mott transition in the impurity band for those donors (i.e., the average distance between impurities $d_c=N_D^{-1/3}>2.5a$, where a is the effective Bohr radius of the donor electron).

The wave function of electron on donor is assumed to be of the s type

$$\varphi(\vec{r})=(\pi a^3)^{-1/2}\exp(-r/a) , \tag{2.10}$$

with a being here a variational parameter to be determined later. We have neglected the field included ellipticity, i.e., $(c\hbar/eH)^{1/2}>a$ is assumed.

Substituting (2.10) into (2.9), we get

$$H_C=\frac{\hbar^2}{2m^*a^2}-\frac{e^2}{\kappa a} + \tfrac{1}{2}\vec{\tau}\cdot\left[\frac{\alpha}{g\mu_B}\int d^3r\,|\varphi(\vec{r})|^2\vec{\mathrm{M}}(\vec{r})+g^*\mu_B\vec{\mathrm{H}}\right] . \tag{2.11}$$

We can rewrite this Hamiltonian in the form

$$H_C=E_D(a)+\tfrac{1}{2}\vec{\tau}\cdot\vec{\Delta} , \tag{2.12}$$

where

$$E_D(a)=\frac{\hbar^2}{2m^*a^2}-\frac{e^2}{\kappa a}$$

is the Coulomb part of the binding energy of the donor electron, and

$$\vec{\Delta}\equiv\vec{\Delta}[\vec{\mathrm{M}}(\vec{r})] =\frac{\alpha}{g\mu_B}\int d^3r\,|\varphi(\vec{r})|^2\vec{\mathrm{M}}(\vec{r})+g^*\mu_B\vec{\mathrm{H}} . \tag{2.13}$$

The value $\Delta\equiv|\vec{\Delta}|$ is the spin splitting of the donor state under the presence of the local magnetization $\vec{\mathrm{M}}(\vec{r})$ within its orbit and in the applied magnetic field $\vec{\mathrm{H}}$. Strictly speaking, it is composed of two

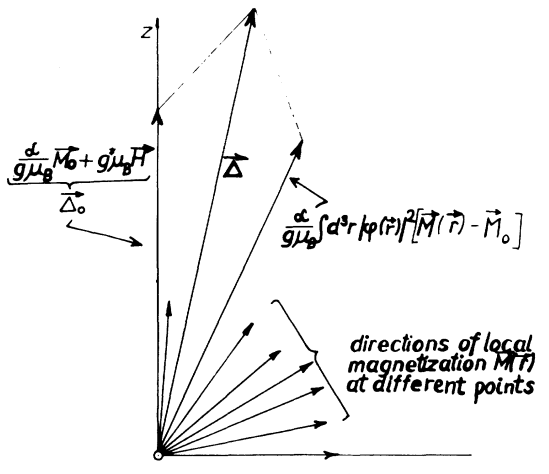

FIG. 2. Components of the vector $\vec{\Delta}$. Magnitude Δ of $\vec{\Delta}$ is the spin splitting of the donor electron.

parts: One is given by the presence of local magnetization $\vec{M}(\vec{r})$ weighted by probability $|\varphi(\vec{r})|^2$ of finding an electron and the other is the ordinary Zeeman splitting.

The direction of $\vec{\Delta}$ supplies a local quantization axis for the electron spin (cf. Fig. 2).

The quantity Δ is of special interest to us because it is available from the spin-flip Raman scattering[11] and the absorption[12] measurements. To calculate it we must determine the shape of the local magnetization $\vec{M}(\vec{r})$. More precisely, due to the presence of thermodynamic fluctuations in the system, we should determine the probability distribution $\mathscr{P}[\vec{M}(\vec{r})]$ of given fluctuation characterized by $\vec{M}(\vec{r})$ to appear, and subsequently get $P(\Delta)$, which determines the intrinsic shape of the spin-flip transition line. This problem is discussed in detail in the next section. However, it is important to note here that the theory can give only the probability distribution of the spin splitting since the cloud surrounding the donor does not order either by itself or by *s-d* coupling at any nonzero temperature. It still does not rule out a possibility of the existence of the most probable value $\bar{\Delta}$ of Δ, as we shall see next.

III. THE PROBABILITY DISTRIBUTION OF THE SPIN SPLITTING

In order to determine the probability distribution $P(\Delta)$ of the spin splitting $\vec{\Delta}$, we have assumed in our previous paper[14] that

$$\vec{M}(\vec{r})=\vec{\eta}\,|\varphi(\vec{r})|^2+\vec{M}_0(\vec{H})\,, \tag{3.1}$$

where $\vec{\eta}$ is the amplitude of the local magnetization caused both by the thermodynamic fluctuations of magnetization and by the molecular field coming from the presence of the donor electron. In this paper we would like to avoid this sort of assumption and treat the whole problem more systematically. Namely, since our aim here is to determine the probability distribution $P(\Delta)$ we construct the free-energy functional [the so-called effective Hamiltonian[16–18] $\mathscr{H}(\vec{\Delta})$], taking into account all possible space profiles of local magnetization $\vec{M}(\vec{r})$ with appropriate weights.

The starting total effective Hamiltonian $\mathscr{H}[\vec{M}(\vec{r})]$ is composed of two parts: the electron part (2.11) and the localized-spins part $\mathscr{H}_s[\vec{M}(\vec{r})]$ having the Ginzburg-Landau form. The latter one is discussed in detail in Appendix A. For a paramagnetic system and in the magnetic field, the lowest-order contribution to the Ginzburg-Landau free-energy functional is

$$\begin{aligned}\mathscr{H}_s[\vec{M}(\vec{r})]=&a_{\parallel}\int d^3r[\vec{M}_{\parallel}(\vec{r})-\vec{M}_0]^2\\&+a_{\perp}\int d^3r\,\vec{M}_{\perp}(\vec{r})^2\\&+\mathscr{C}\int d^3r[\nabla\vec{M}(\vec{r})]^2\,,\end{aligned} \tag{3.2}$$

with $\vec{M}_{\parallel}$ and $\vec{M}_{\perp}$ being the parallel and perpendicular components of $\vec{M}(\vec{r})$ with respect to the field-induced macroscopic magnetization $\vec{M}_0$,

$$a_{\parallel}=\frac{1}{2}\left[\frac{\partial M_0}{\partial H}\right]^{-1},\quad a_{\perp}=\frac{1}{2}\left[\frac{M_0}{H}\right]^{-1},$$

and $\mathscr{C}$ being the exchange stiffness constant. In (3.2) we have included only the terms quadratic in magnetization since we limit ourselves to the case when the contributions coming from the presence of the donor electron and from the fluctuations are small compared to the saturation value M_s of M_0.

The probability distribution of $\vec{M}(\vec{r})$ is defined through the canonical distribution summed up over donor spin degrees of freedom

$$\mathscr{P}[\vec{M}(\vec{r})]=C\operatorname*{Tr}_{\{\tau_z\}}\exp\left[-\frac{\mathscr{H}[\vec{M}(\vec{r})]}{k_BT}\right], \tag{3.3}$$

where C is a normalizing constant, and Tr means summation over $\tau_z=\pm1$ for the donor electron when the direction of $\vec{\Delta}$ is chosen as a quantization axis. Then, the explicit form of (3.3) is

$$\begin{aligned}\mathscr{P}[\vec{M}(\vec{r})]=&C\exp\left[-\frac{\mathscr{H}_s[\vec{M}(\vec{r})]}{k_BT}\right]\\&\times2\cosh\left[\frac{\Delta[\vec{M}(\vec{r})]}{2k_BT}\right].\end{aligned} \tag{3.4}$$

The probability distribution $P(\vec{\Delta})$ of the spin splitting Δ is obtained from (3.3) by the appropriate change of variables

$$P(\vec{\Delta})=\int\mathscr{P}[\vec{M}(\vec{r})]\delta\{\vec{\Delta}-\vec{\Delta}[\vec{M}(\vec{r})]\}\mathscr{D}\vec{M}(\vec{r})\,. \tag{3.5}$$

The meaning of the transformation (3.5) is as follows. We would like to calculate the contributions coming from all profiles of magnetization, $\{\vec{M}(\vec{r})\}$, giving a contribution to given $\vec{\Delta}$ of the spin splitting. This necessitates the functional integration over all possible "paths" of $\vec{M}(\vec{r})$ with the weighting factor $\mathscr{P}[\vec{M}(\vec{r})]$.

Therefore, the transformed effective Hamiltonian can be defined (up to an irrelevant constant) by

$$\mathscr{H}(\vec{\Delta}) = -k_B T \ln P(\vec{\Delta}) \,. \tag{3.6}$$

In order to perform the functional integration contained in (3.5), we develop first the Fourier series of the involved quantities, i.e.,

$$\vec{M}(\vec{r}) - \vec{M}_0 = \frac{1}{\sqrt{V}} \sum_{\vec{q}} \vec{\eta}_{\vec{q}} \exp(i\vec{q}\cdot\vec{r}) \tag{3.7}$$

and

$$|\varphi(\vec{r})|^2 = \frac{1}{\sqrt{V}} \sum_{\vec{q}} b_{\vec{q}} \exp(i\vec{q}\cdot\vec{r}) \,, \tag{3.8}$$

where V is total volume of the system. Then the effective Hamiltonian in the new representation becomes

$$\mathscr{H}\{\vec{\eta}_{\vec{q}}\} = \sum_{\vec{q}}{}' [\chi_{\perp}^{-1}(\vec{q}) |\vec{\eta}_{\perp\vec{q}}|^2 + \chi_{\parallel}^{-1}(\vec{q}) |\vec{\eta}_{\parallel\vec{q}}|^2] - k_B T \ln \left[2\cosh \left[\left| \frac{\vec{\Delta}_0}{2k_B T} + \frac{\alpha}{g\mu_B k_B T} \sum_{\vec{q}}{}' \mathrm{Re}(\vec{\eta}_{\vec{q}} b^*_{\vec{q}}) \right| \right] \right] , \tag{3.9}$$

where $\sum'_{\vec{q}}$ means that the summation is taken over half of the first Brillouin zone [this is because $\vec{M}(\vec{r})$ is a real function so $\vec{\eta}_{\vec{q}} = \vec{\eta}^*_{-\vec{q}}$, and thus $\vec{\eta}_{\vec{q}}$ and $\vec{\eta}_{-\vec{q}}$ are not independent variables],

$$\chi_{\perp}^{-1}(\vec{q}) = 2(a_{\perp} + \mathscr{C}\vec{q}^{\,2}) \,, \tag{3.10}$$

$$\chi_{\parallel}^{-1}(q) = 2(a_{\parallel} + \mathscr{C}\vec{q}^{\,2}) \,, \tag{3.11}$$

and

$$\vec{\Delta}_0 = \frac{\alpha}{g\mu_B} \vec{M}_0 + g^* \mu_B \vec{H} \,. \tag{3.12}$$

Hence the new effective Hamiltonian (3.6) in the same representation takes the form ($\vec{\eta}_{\vec{q}} \equiv \vec{\eta}'_{\vec{q}} + i\vec{\eta}''_{\vec{q}}$)

$$\mathscr{H}(\vec{\Delta}) = -k_B T \ln \left[2\cosh \left[\frac{\Delta}{2k_B T} \right] \int_{-\infty}^{\infty} \left[\prod_{\vec{q}}{}' d^3\eta'_{\vec{q}} d^3\eta''_{\vec{q}} \right] \times \exp \left[-\frac{\mathscr{H}_s\{\vec{\eta}_{\vec{q}}\}}{k_B T} \right] \delta \left[\vec{\Delta} - \vec{\Delta}_0 - \frac{2\alpha}{g\mu_B} \sum_{\vec{q}}{}' \mathrm{Re}(\vec{\eta}_{\vec{q}} \cdot b^*_{\vec{q}}) \right] \right] + E_D(a) \,. \tag{3.13}$$

After some algebra (for details see Appendix B) we get up to an additive constant

$$\mathscr{H}(\vec{\Delta}) = -k_B T \ln \left[2\cosh \left[\frac{\Delta}{2k_B T} \right] \right] + \frac{\vec{\Delta}_{\perp}^{\,2}}{8\epsilon_{p\perp}} + \frac{(\vec{\Delta}_{\parallel} - \vec{\Delta}_0)^2}{8\epsilon_{p\parallel}} + E_D(a) \tag{3.14}$$

with

$$\epsilon_{p\perp,\parallel} = \frac{\alpha^2}{2(g\mu_B)^2} \sum_{\vec{q}}{}' \chi_{\perp,\parallel}(\vec{q}) |b_{\vec{q}}|^2 \,, \tag{3.15}$$

where $\vec{\Delta}_{\perp}$ and $\vec{\Delta}_{\parallel}$ are the components of $\vec{\Delta}$ perpendicular and parallel to $\vec{\Delta}_0$, respectively. Since in the further analysis we limit ourselves to the case of dilute paramagnetic system, one can assume that the gradient term in the expansion (3.2) is unimportant ($\mathscr{C} = 0$). Additionally, neglecting the field-induced anisotropy in [i.e., assuming that $\frac{1}{2}a_{\perp}^{-1} = \frac{1}{2}a_{\parallel}^{-1} \equiv \chi = (\partial M_0/\partial H)$], we get

$$\mathscr{H}(\vec{\Delta}) = -k_B T \ln \left[2\cosh \left[\frac{\Delta}{2k_B T} \right] \right] + \frac{(\vec{\Delta} - \vec{\Delta}_0)^2}{8\epsilon_p} + E_D(a) \,, \tag{3.16}$$

with

$$\epsilon_p = \frac{\alpha^2 \chi}{2(g\mu_B)^2} \sum_{\vec{q}}{}' |b_{\vec{q}}|^2 \,. \tag{3.17}$$

Assuming that the average distance between the magnetic impurities is much smaller than the Bohr radius, we get for the hydrogeniclike wave function (2.10)

$$\epsilon_p = \frac{\alpha^2 \chi}{32\pi a^3 (g\mu_B)^2} . \tag{3.18}$$

The result (3.16) with ϵ_p given by (3.18) coincides with the one obtained previously[14] employing the ansatz (3.1). The effective Hamiltonian (3.16) will be used in the following discussion of the spin-splitting distribution and its most probable value $\bar{\Delta}$. The latter will be discussed first in the mean-field approximation (MFA). The more general case of the effective Hamiltonian (3.14) with $a_\perp \neq a_{||}$ but with $\mathscr{C}=0$ is discussed briefly in Appendix C.

A. Mean-field approximation

To have a contact with the mean-field approach devised by other authors,[1,5,7] we note that in that approximation the expected value $\bar{\Delta}$ of spin splitting Δ is obtained by a minimalization of the effective Hamiltonian $\mathscr{H}(\vec{\Delta})$. In other words, in the MFA we take only one particular value of Δ when describing the properties of the system. The specific value of Δ is taken as the one which corresponds to the leading term in the partition function.

Then, one gets the following equation for $\bar{\Delta}$:

$$\bar{\Delta} - \Delta_0 - 2\epsilon_p \tanh\left[\frac{\bar{\Delta}}{2k_B T}\right] = 0 . \tag{3.19}$$

For either $T \to 0$ or strong fields ($\Delta_0 > \epsilon_p, k_B T$), we get $\bar{\Delta} \simeq \Delta_0 + 2\epsilon_p$.

For $H=0$ ($\Delta_0=0$), Eq. (3.19) has a form of the mean-field equation for magnetization. Expanding $\tanh x \simeq x - x^3/3$ for small $\Delta/k_B T$, we get

$$\bar{\Delta} = k_B T \left[\frac{12}{\epsilon_p}(\epsilon_p - k_B T)\right]^{1/2} . \tag{3.20}$$

So, we get the classical critical exponent $\beta = \frac{1}{2}$ for the temperature dependence of the zero-field splitting. In particular, there exists a critical temperature $T_p = \epsilon_p / k_B$ at which spins of the cloud surrounding the donor get disordered. The equation determining the effective Bohr radius a in the region where $\bar{\Delta}(T)$ is given by (3.20) can be obtained substituting (3.20) into (3.16) and setting $\partial \mathscr{H}(\bar{\Delta})/\partial a = 0$.

We then get an equation for variable a

$$-\frac{\hbar^2}{m^*} + \frac{e^2}{\kappa} a + \frac{1}{48} a^2 (\epsilon_p - k_B T) = 0 , \tag{3.21}$$

thus, as $T \to T_p$,

$$a \to a_B = \frac{\hbar^2 \kappa}{m^* e^2} ,$$

i.e., above T_p we get the Bohr radius for an ordinary donor level.

To visualize critical behavior of a BMP state in the mean-field approximation in a more direct way have calculated the static susceptibility of our system. Namely, expanding $\tanh(x) \simeq x$ in (3.19) for $\Delta_0 \neq 0$, we get for $T \geq T_p$

$$\bar{\Delta} = \frac{\Delta_0}{1 - \epsilon_p / k_B T} = H \frac{\alpha\chi / g\mu_B + g^* \mu_B}{1 - \epsilon_p / k_B T} . \tag{3.22}$$

We see that the cloud susceptibility diverges as $k_B T \to \epsilon_p$, even though the susceptibility χ of a dilute paramagnet as a whole does not. So, the presence of a donor electron coupled through *s-d* exchange with spins leads to a continuous phase transition at a finite temperature $T_p = \epsilon_p / k_B$. One can expect that this result is simply untrue for this system (BMP) which is of finite size. We will show in the following that the inclusion of the thermodynamic fluctuations washes out this transition entirely.

For the sake of completeness as well as for a comparison with a better approach that we are going to study next, we have plotted in Fig. 3 the field dependence of $\bar{\Delta}$. The parameters taken are those for $Cd_{0.95}Mn_{0.05}Se$ (cf. Appendix D).

The reason why we should include fluctuations in

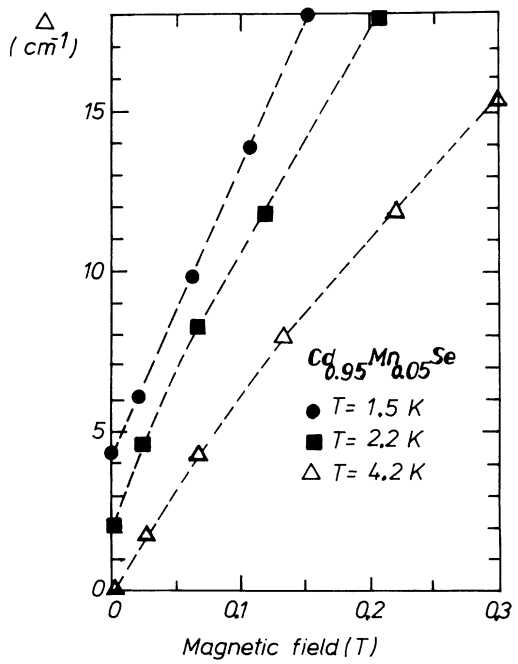

FIG. 3. Applied field dependence of the value of the spin splitting ($\bar{\Delta}$) in the MFA. The parameters are those of $Cd_{1-x}Mn_xSe$ with $x=0.05$ (cf. Appendix D).

the subsystem of spins is very simple. Namely, a BMP composed of the donor electron and a cloud of magnetization surrounding it is a system of finite size embedded in a heat bath.

Fluctuations of magnetization beyond the critical region are also of a finite size. So, they can have an important contribution to the localized states even though their part in macroscopic magnetization of the whole sample may be negligible. Additionally, fluctuations may show themselves at relatively low temperature because the dilute system of spins below the percolation threshold does not order by itself at any finite temperature.

To incorporate the thermodynamical fluctuations of magnetization into our scheme, we proceed as follows. The probability distribution of fluctuation occurence at given temperature and volume of the system is [cf. Eq. (3.6)]

$$P(\vec{\Delta})=C\exp\left[-\frac{\mathscr{H}(\vec{\Delta})}{k_BT}\right]. \tag{3.23}$$

The normalization constant is to be found from

$$C^{-1}=\int d^3\Delta\exp\left[-\frac{\mathscr{H}(\vec{\Delta})}{k_BT}\right]. \tag{3.24}$$

Since the spin splitting of the electron is determined by $|\vec{\Delta}|$, we integrate over polar (θ) and asimuthal (φ) angles.

B. Inclusion of thermodynamic fluctuations

At finite temperature the region of parameter Δ beyond the minimum of $\mathscr{H}(\vec{\Delta})$ is also accessible to the system. This is due to the presence of the thermodynamic fluctuations of the local magnetization $\vec{M}(\vec{r})$ and the finite size ($\sim a$) of the BMP.

We then get the probability distribution of spin splitting [we integrate (3.23) over the angles]

$$P(\Delta)=C'\Delta\sinh\left[\frac{\Delta\Delta_0}{4\epsilon_pk_BT}\right]\cosh\left[\frac{\Delta}{2k_BT}\right]\times\exp\left[-\frac{\Delta^2}{8\epsilon_pk_BT}\right], \tag{3.25}$$

where

$$C'=C\frac{32\pi\epsilon_pk_BT}{\Delta_0}\exp\left[-\frac{\Delta_0^2}{8\epsilon_pk_BT}\right]\exp\left[-\frac{E_D(a)}{k_BT}\right]. \tag{3.26}$$

The formula (3.25) gives the probability distribution of the spin splitting Δ in the presence of applied field H; i.e.,

$$\Delta_0=\frac{\alpha}{g\mu_B}M_0(H)+g^*\mu_BH\neq0\ .$$

In the limit $H\to0$ we get

$$P(\Delta)\,|_{H=0}=C''\Delta^2\exp\left[-\frac{\Delta^2}{8\epsilon_pk_BT}\right]\cosh\left[\frac{\Delta}{2k_BT}\right]. \tag{3.27}$$

This formula can be interpreted as follows. The factor Δ^2 comes from the density of states in space of $\vec{\Delta}$ with given $|\vec{\Delta}|$. The next factor is a Gaussian distribution of the local magnetization of the cloud treated classically and accompanying the donor electron. The last factor comes from the *s-d* coupling of spins with the donor electron. Because $\cosh x>1$, the *s-d* coupling enhances the magnitude of the spin splitting created by the fluctuation.

C. The most probable value of the spin splitting

The most probable configuration $\bar{\Delta}$ of Δ is found from the condition

$$\left[\frac{dP(\Delta)}{d\Delta}\right]_{\bar{\Delta}}=0\ ,$$

which leads to

$$2k_BT-\bar{\Delta}\frac{\partial}{\partial\Delta}\mathscr{H}(\Delta)\,|_{\bar{\Delta}}=0\ . \tag{3.28}$$

We see that the minimal work involved to create a fluctuation[17] of amplitude $\bar{\Delta}$ is equibalanced by the thermal motion ($\sim k_BT$). So, the results of this section and those of mean-field approach coincide only for $T=0$. Equation (3.28) has the following form:

$$\bar{\Delta}^2-2\epsilon_p\bar{\Delta}\tanh\left[\frac{\bar{\Delta}}{2k_BT}\right]-\bar{\Delta}\Delta_0\coth\left[\frac{\bar{\Delta}\Delta_0}{4\epsilon_pk_BT}\right]-4\epsilon_pk_BT=0\ . \tag{3.29}$$

The parameter ϵ_p appearing in this equation still contains unspecified effective Bohr radius a [cf. (3.18)]. It can be found by minimizing the free energy ΔF of the system. The explicit expression for ΔF, which includes the fluctuations, will be given in the next section. Before analyzing Eq. (3.29) numerically, we will discuss some particular cases which can be solved analytically.

1. *Case A: $H=0$*

Taking in (3.27) first the limit $\Delta_0\to0$ and then $T\to0$, we get $\bar{\Delta}=2\epsilon_p$. This result coincides with the MFA. Furthermore, taking into account the

term in T in (3.29) we get the low-temperature limit

$$\bar{\Delta}=\epsilon_p\left[1+\left[1+\frac{8k_BT}{\epsilon_p}\right]^{1/2}\right]. \tag{3.30}$$

In the opposite limit $T\to\infty$ (i.e., for $\epsilon_p \ll k_BT$), we get

$$\bar{\Delta}^2=\frac{8k_BT\epsilon_p}{1-\epsilon_p/k_BT}\simeq 8\epsilon_p k_BT=\frac{k_BT}{4\pi a^3}\frac{\alpha^2}{(g\mu_B)^2}. \tag{3.31}$$

Noting that

$$\bar{\Delta}=\frac{\alpha}{g\mu_B}\langle M\rangle,$$

where $\langle M\rangle$ is an average magnetization within the Bohr radius, the above result can be compared with the most probable amplitude of fluctuation of macroscopic magnetization[16,18] in the paramagnetic region

$$\langle M^2\rangle=\frac{2k_BT\chi}{\tilde{V}}, \tag{3.32}$$

where $\tilde{V}$ is volume of the system under consideration. This means that the spin splitting $\bar{\Delta}$ in the high-temperature region $k_BT\gg\epsilon_p$ is solely due to thermodynamic fluctuations as has been shown by an example of simple reasoning.[14]

In particular, because for $T\to\infty$, $\chi\sim 1/T$, we see that

$$\lim_{T\to\infty} k_BT\chi=C_M>0,$$

where C_M is the Curie constant of the susceptibility. Hence, the spin-flip energy is nonzero even for $k_BT\gg\epsilon_p$, i.e., far above the mean-field critical temperature T_p. In other words, the donor electrons lowers its energy, aligning its spin along the instantaneous magnetization of the cloud. Such a situation certainly takes place if the relaxation time for the cloud decay is both much longer than the period of the Larmor precession of the electron spin in the effective field produced by this fluctuation and larger than the spin-relaxation time of the donor electron. It has been pointed out before (cf. Sec. II) that since the polaron is large the individual spins may relax much faster than the whole cloud.

2. *Case B: $H\neq 0$, $T\to 0$ (i.e., $\epsilon_p\gg k_BT$)*

Now we will analyze fully Eq. (3.29), first for $T\to 0$. In strong fields, i.e., for

$$\frac{\bar{\Delta}\Delta_0}{4\epsilon_p k_BT}\gg 1,$$

we have

$$\bar{\Delta}\simeq\tfrac{1}{2}\{\Delta_0+2\epsilon_p+[(\Delta_0+2\epsilon_p)^2+16\epsilon_p k_BT]^{1/2}\}$$
$$\simeq 2\epsilon_p+\Delta_0+\frac{4\epsilon_p k_BT}{\Delta_0+2\epsilon_p}. \tag{3.33}$$

For $T=0$ or $H\to\infty$ Eq. (3.33) reduces to mean-field result. We see that the spin splitting

$$\bar{\Delta}\sim\Delta_0=\frac{\alpha}{g\mu_B}M_0+g^*\mu_BH.$$

So, the field dependences of splitting follows roughly the Brillouin curve for the strong fields.

For low fields ($H\to 0$), (3.29) can be written as

$$\bar{\Delta}^2-2\epsilon_p\bar{\Delta}\tanh\left[\frac{\bar{\Delta}}{2k_BT}\right]-\frac{1}{12}\frac{\bar{\Delta}^2\Delta_0^2}{k_BT\epsilon_p}-8\epsilon_p k_BT=0. \tag{3.34}$$

So, for $\Delta_0^2/\epsilon_p k_BT\ll 1$ we have

$$\bar{\Delta}\simeq\epsilon_p\left[1+\left[1+\frac{8k_BT}{\epsilon_p}\right]^{1/2}\right]. \tag{3.35}$$

$\bar{\Delta}$ in this region depends only weakly on H (the region of plateau). So the interpolation formula for $\bar{\Delta}(H)$ should give a plateau of $\bar{\Delta}(H)$ first, then a linear dependence ($\bar{\Delta}\sim H$) and the approximate Brillouin law $\bar{\Delta}\sim B_{5/2}[9\mu_BH/k_B(T+T_0)]$ as $H\to\infty$.

3. *Case C: $H\neq 0$, $T\to\infty$ (i.e., $\epsilon_p\ll k_BT$)*

For $T\to\infty$ and for strong fields, i.e., for

$$\frac{\Delta_0^2}{4\epsilon_p k_BT}\gg 1,$$

but

$$\frac{\Delta_0}{2k_BT}\ll 1,$$

we have

$$\bar{\Delta}^2\left[1-\frac{\epsilon_p}{k_BT}\right]-\bar{\Delta}\Delta_0-4\epsilon_p k_BT=0. \tag{3.36}$$

Since $\epsilon_p/k_BT\ll 1$,

$$\bar{\Delta}\simeq\frac{\Delta_0}{2}+\left[\frac{\Delta_0^2}{4}+4\epsilon_p k_BT\right]^{1/2}. \tag{3.37}$$

Comparing (3.37) with (3.33) we see that the latter equation is a good first-order formula for a strong field in the full temperature range.

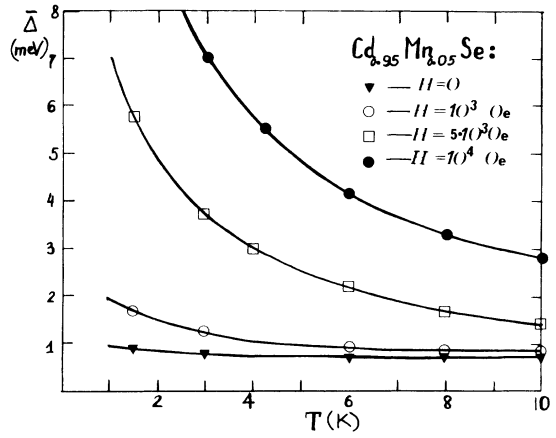

FIG. 4. Most probable value $\bar{\Delta}$ of the spin splitting as a function of temperature T for various fields as specified. The parameters are those for $Cd_{1-x}Mn_xSe$ with $x=0.05$.

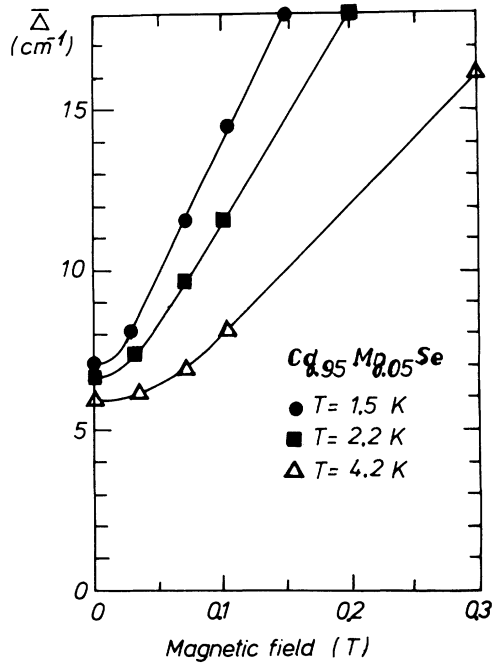

FIG. 5. Same as in Fig. 4 but as a function of applied field. The temperatures are specified. Note that points on the curves are representing theory.

For low fields, starting from (3.34) we get

$$\bar{\Delta}^2=8\epsilon_p k_B T\Big/\left[1-\frac{\epsilon_p}{k_B T}-\frac{1}{12}\frac{\Delta_0^2}{k_B T\epsilon_p}\right]$$
$$\simeq 8\epsilon_p k_B T\left[1+\frac{\epsilon_p}{k_B T}+\frac{1}{12}\frac{\Delta_0^2}{k_B T\epsilon_p}\right]. \quad (3.38)$$

So, we see that Eq. (3.35) is a good first-order interpolation formula between the region $T\to 0$ and $T\to\infty$ for low magnetic field. In order to illustrate the temperature and field dependences of the most probable value $\bar{\Delta}$ of the spin splitting $\bar{\Delta}=\bar{\Delta}(T,H)$ we have calculated it numerically. The results are shown in Figs. 4 and 5. The parameters of $Cd_{1-x}Mn_xSe$ are as specified in Appendix D. The results shown in Figs. 4 and 5 will be discussed in connection with the spin-flip Raman scattering experiments.[11] However, one should also include the occupational probabilities of the spin-split levels when calculating the optical transition probabilities (see Sec. V).

IV. THERMODYNAMICS

Suppose we have N_D isolated and occupied donors per unit volume. Then one can calculate a contribution ΔF to the free energy of the system, introduced by the presence of the donor electron which had formed the BMP. It is defined as a difference between the free energy when donor is present and the spin part when donor is absent, i.e.,

$$\Delta F=-k_B T\ln\left[\operatorname{Tr}_{\{\tau^z\}}\int d^3\Delta\exp\left[-\frac{1}{k_B T}(\mathscr{H}_s+\mathscr{H}_c)\right]\right]+k_B T\ln\left[\int d^3\Delta\exp\left[-\frac{\mathscr{H}_s}{k_B T}\right]\right]. \quad (4.1)$$

Substituting (3.16) for the effective Hamiltonian $\mathscr{H}_s+\mathscr{H}_c$ and (3.2) transformed to $\vec{\Delta}$ variable for $\mathscr{H}_s$, we find

$$\Delta F=\frac{\hbar^2}{2m^*a^2}-\frac{e^2}{\kappa a}-\frac{\epsilon_p}{2}$$
$$-k_B T\ln\left[2\cosh\left[\frac{\Delta_0}{2k_B T}\right]+\frac{4\epsilon_p}{\Delta_0}\sinh\left[\frac{\Delta_0}{2k_B T}\right]\right]. \quad (4.2)$$

This formula does not depend on Δ and is the one we minimize with respect to a to get the effective Bohr radius. The equation for a thus obtained must be solved numerically in the general case. However, for both low and high temperatures ($\epsilon_p\gg k_B T$ and $\epsilon_p\ll k_B T$, respectively) and for the applied field equal to zero, we can get analytical results. Namely, for $T\to 0$,

$$\Delta F=-\epsilon_p/2+E_D(a)-k_B T\ln 2,$$

while in the opposite limit

$$\Delta F=-\tfrac{3}{2}\epsilon_p+E_D(a)-k_BT\ln 2 .$$

Then for $\epsilon_p/k_BT\gg 1$ $(T\to 0)$, we get

$$a\simeq\frac{a_B}{2}\left[1+\left[1-3\frac{\epsilon_p(a_B)}{E_D(a_B)}\right]^{1/2}\right], \tag{4.3}$$

while for $\epsilon_p/k_BT\ll 1$ $(T\to\infty)$

$$a\simeq\frac{a_B}{2}\left[1+\left[1-9\frac{\epsilon_p(a_B)}{E_D(a_B)}\right]^{1/2}\right], \tag{4.4}$$

where

$$\epsilon_p(a_B)=\frac{\alpha^2\chi}{(g\mu_B)^2 32\pi a_B^3}, \tag{4.5}$$

$$E_D(a_B)=\frac{e^2}{2\kappa a_B}, \tag{4.6}$$

and $a_B=\hbar^2\kappa/m^*e^2$ is the Bohr radius of the first orbit when the dielectric constant is κ and the electron mass is m^*. Note that for the parameters characterizing $Cd_{1-x}Mn_xSe$ (cf. Appendix D) the correction to the effective Bohr radius a coming from the s-d coupling is up to 2% of a_B. Thus to a good approximation one can take $a=a_B$.

Having calculated the BMP contribution ΔF to the free energy of the whole system, one can calculate the various thermodynamic quantities. For example, the static magnetic susceptibility of the BMP

$$\chi_d=-N_D\left[\frac{\partial^2\Delta F}{\partial H^2}\right]_{T,H=0}. \tag{4.7}$$

is

$$\chi_d=\frac{N_D\mu_B^2}{4k_BT}\left[g^*+\frac{\alpha\chi}{g\mu_B^2}\right]^2 \times\left[\left[1+\frac{\epsilon_p}{3k_BT}\right]\Big/\left[1+\frac{\epsilon_p}{k_BT}\right]\right]. \tag{4.8}$$

Hence at high temperature ($\epsilon_p/k_BT\ll 1$), the total susceptibility is composed of two parts: the unperturbed spin susceptibility χ and the susceptibility of the localized donor electron (the standard Curie law) with the effective Landé factor $g_{\rm eff}=g^*+\alpha\chi/g\mu_B^2$. Also from (4.8) we see that the critical behavior obtained in the MFA [cf. (3.22)] is washed out completely by fluctuations. However, at low temperature ($\epsilon_p/k_BT\ll 1$) we obtain, unlike in the MFA, a finite value of χ_d even though the spin splitting is much larger than k_BT. This is because the applied field aligns partially the quantization axes of individual BMP's.

We calculate also the entropy per donor

$$\Delta S=-\frac{\partial\Delta F}{\partial T}, \tag{4.9}$$

which is for $H=0$

$$\Delta S=k_B\ln 2+k_B\ln\left[1+\frac{\epsilon_p}{k_BT}\right] -\frac{k_B\epsilon_p}{k_BT+\epsilon_p}\left[1-\left[3+\frac{\epsilon_p}{k_BT}\frac{T}{2\chi}\frac{\partial\chi}{\partial T}\right]\right]. \tag{4.10}$$

Having the entropy, one can calculate the internal energy ΔU and get

$$\Delta U=E_D(a)-\frac{\epsilon_p}{2} +\frac{3+\epsilon_p/k_BT}{1+\epsilon_p/k_BT}\left[1-\frac{T}{\chi}\frac{\partial\chi}{\partial T}\right]. \tag{4.11}$$

This quantity gives us the specific heat $C_v=(\partial\Delta U/\partial T)_v$. In calculating C_v we assume that the effective Bohr radius is independent of temperature. We then get

$$C_v=\frac{\epsilon_p}{T}\left\{\left[1+2\left[1+\frac{\epsilon_p}{k_BT}\right]^{-1}\right]\frac{T^2}{2\chi}\frac{\partial^2\chi}{\partial T^2} -\frac{\epsilon_p}{k_BT}\left[\frac{1-(T/\chi)(\partial\chi/\partial T)}{1+\epsilon_p/k_BT}\right]^2\right\}N_D . \tag{4.12}$$

This formula is not very transparent. For $T\gg T_0$ (i.e., for $\epsilon_p/k_BT\ll 1$), however, and assuming that $\chi=C_M/(T+T_0)$, we get

$$C_v=\frac{N_D\epsilon_p}{T\left[1+\frac{\epsilon_p}{k_BT}\right]^2}\left[\left[\frac{\epsilon_p}{k_BT}\right]^2+3\right]. \tag{4.13}$$

Also, we get asymptotically $C_v<0$ as $T\ll T_0\sim 1$ K. One must be careful in taking the last result too seriously because for very low temperatures the Curie-Weiss law for χ may not be fulfilled.

V. COMPARISON WITH EXPERIMENT

The direct optical transition between spin-split levels of the donor state is not allowed by the selection rules. However, it can be allowed either via involvement of intermediate states (as happens in spin-flip Raman experiments) or if the s-type wave

function has an admixture of higher ones ($2p$, $3p$, etc.). The transition involving the spin flip of the electron on the donor level will be influenced by the direction of applied magnetic field with respect to the geometry of light beam (s).

To show the usefulness of the concept of the BMP in explaining the experimental results, we will discuss the data of Nawrocki *et al.*[11] concerning the spin-flip Raman scattering in $Cd_{0.95}Mn_{0.05}Se$. It should be emphasized that this method, as well as recent optical absorption data of Dobrowolska *et al.*,[12] provides a direct measurement of the spin splitting $\Delta(T,H)$. In the following we concentrate on the former experimental results only. The shape of the spin-flip Raman line $I(\Delta)$ is represented by $P(\Delta)$, given by Eq. (3.25), multiplied by probability that the donor electron has its spin aligned or antialigned with the direction of effective field $\Delta(T,H)$ acting upon it

$$I(\Delta)=\bar{C}P(\Delta)\exp\left[\pm\frac{\Delta}{2k_BT}\right]\left[1\Big/2\cosh\left[\frac{\Delta}{2k_BT}\right]\right], \tag{5.1}$$

where $\bar{C}$ is a constant related to the scattering cross section, and $\pm$ refers to the Stokes and anti-Stokes components of the line, respectively. The peak position of the line is therefore supplied by the condition

$$\left.\frac{dI(\Delta)}{d\Delta}\right|_{\Delta=\tilde{\Delta}}=0\,. \tag{5.2}$$

Then the appropriate equation for $\tilde{\Delta}$ is

$$\tilde{\Delta}^2\mp 2\epsilon_p\tilde{\Delta}-\tilde{\Delta}\Delta_0\coth\left[\frac{\tilde{\Delta}\Delta_0}{4\epsilon_p k_BT}\right]-4\epsilon_p k_BT=0\,, \tag{5.3}$$

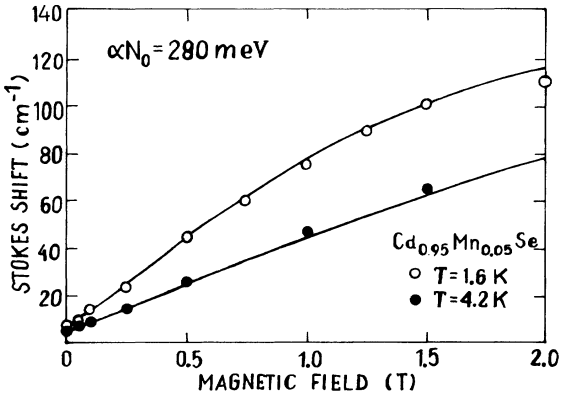

FIG. 6. Applied field dependence of the Stokes line position for $Cd_{0.95}Mn_{0.05}Se$ in the high-field region. Experimental points are taken from Ref. 11, while the continuous line represents the theoretical dependence of $\tilde{\Delta}$ vs H for $\alpha N_0=280$ meV.

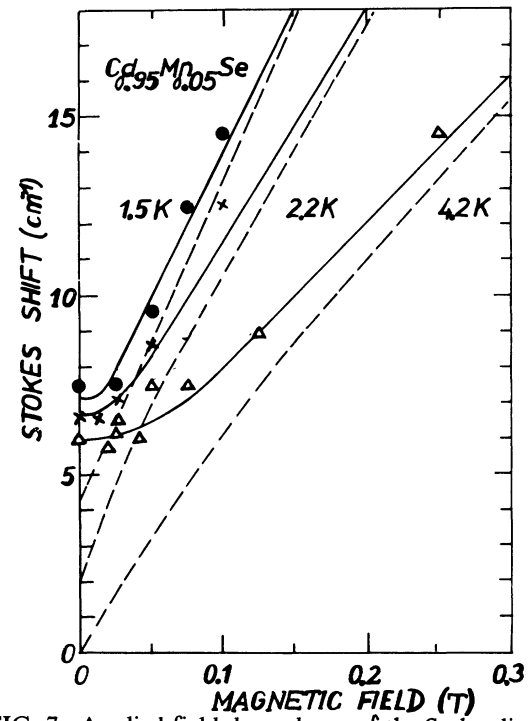

FIG. 7. Applied field dependence of the Stokes line position for $Cd_{1-x}Mn_xSe$ with $x=0.05$ in the low fields and at various temperatures. Experimental points, after Ref. 11. Solid lines, theory including fluctuations. Dashed lines, MFA.

where $\mp$ corresponds as before to the Stokes and anti-Stokes components. Equation (5.3) predicts an asymmetry between the components with respect to the central line. This prediction differs with that given previously,[14] which assumes that all donors are aligned with $\vec{\Delta}$ in the initial state.[19] Nonetheless, the difference between the peak position obtained from (5.3) and the most probable value $\bar{\Delta}$ of spin splitting given by Eq. (3.29) should be small, particularly for $\epsilon_p \gg k_BT$. In the high-temperature regime ($\epsilon_p/k_BT \ll 1$) and $\Delta_0=0$, we have

$$\tilde{\Delta}=\pm\epsilon_p+(\epsilon_p^2+8\epsilon_p k_BT)^{1/2}\,. \tag{5.4}$$

This differs by ϵ_p with the value $\bar{\Delta}$ obtained in the same limit [cf. (3.38)]. In the opposite limit, $\epsilon_p/k_BT \gg 1$, we get from (5.3) the result $\tilde{\Delta}=\bar{\Delta}$, where $\bar{\Delta}$ is given by (3.35).

The quantitative comparison of our numerical results obtained from solving Eq. (5.3) and the effective Bohr radius adjustment [minimization of (4.2)], with the experimental data of Nawrocki *et al.*,[11] is given in Figs. 6 and 7. In Fig. 6 we have plotted the field dependence of the Stokes line for $Cd_{0.95}Mn_{0.05}Se$. These results were used to determine the value of the s-d exchange constant $\alpha N_0=280$ meV. The overall field dependence, particularly for stronger fields, follows the Brillouin curve (D1) (cf. Appendix D), as expected from the

MFA picture of the donor spin splitting. However, in the region of relatively small fields $H \lesssim 5$ kOe there is an essential departure from the Brillouin law (D1). Namely, the spin splitting levels off as $H \to 0$ at a nonzero value for the whole temperature range studied. The field dependence of the position of the Stokes component in that region is shown in Fig. 7.

From the comparison with the data we draw a conclusion that our theory provides an appropriate quantitative description of the spin splitting for the donor electron, without invoking the concept of the long-range magnetic order in these dilute magnetic systems. For field $H \to 0$, the donor electron aligns its spin with the direction of magnetization coming from both the effective field provided by the *s-d* coupling and by thermodynamic fluctuations of magnetization of the surrounding cloud of spins. The former effect is predominant at low temperatures ($T \lesssim 1.5$ K), while the latter one is predominant at higher temperatures ($T \gtrsim 4.2$ K).

The contribution to the peak position coming from the fluctuations decreases with increasing field. This is because applied magnetic field induces a macroscopic magnetization which fixes the quantization axis for donor spins and thus the effect of fluctuations averages out to zero. The field dependence in the low-field region is approximately parabolic and concave [cf. Eq. (3.38)]. Eventually, for still stronger fields the fluctuations are suppressed, and Δ approaches the value $\Delta_0 + 2\epsilon_p$ [cf. Eq. (3.33)], i.e., the mean-field value. It is worth noting that the effect of fluctuations on the BMP discussed in this paper is of importance when analyzing the data concerning the transport properties of $Cd_{1-x}Mn_xSe$ (Ref. 20) and $Cd_{1-x}Mn_xTe$ (Ref. 21).

VI. DISCUSSION

Let us recapitulate the main assumptions of our work. Firstly, we have taken into account the polarization of the cloud of spins, treating the spins as classical vectors. Also, the polarization of the cloud is regarded as small with respect to its saturation value. Hence the continuous medium approximation is used throughout the paper. Within this approximation the magnetic properties of the medium are characterized by susceptibility $\chi(T,H)$ available from independent measurements.

From (4.3) we see that we can treat the donor as creating a large polaron provided that a_B is large, i.e., either κ is large or m^* is small, or both. Additionally, it must be true that

$$\epsilon_p(a_B)/E_D(a_B) \ll \tfrac{1}{3} ,$$

i.e., the magnetic energy of the donor electron is much less than its electrostatic energy.

Moreover, we have supposed that the neighbor donor states do not overlap appreciably with each other. This means that we are well below the critical concentration for the Mott transition. The magnetic (*s-d*) interaction shrinks the donor orbit so it shifts the transition to a slightly higher donor concentration. Also, we neglect the exchange interactions between electrons placed on neighboring donors.

Furthermore, the thermal activation to the conduction band has been neglected. In general, the number of occupied donors depends on the temperature, $N_D = N_D(T)$, according to the thermal-activation law, but with magnetic free energy $\sim -\epsilon_p/2$ included.

Each of these assumptions can, in principle, be eliminated. In particular, one can consider the influence of fluctuations on the BMP in the ferromagnetic case. The procedure is quite analogous well above the Curie temperature T_C [with $\chi = C_M/(T-\Theta)$ for $H=0$]. However, around T_C one should include the higher-order terms in the Ginzburg-Landau functional (3.2) for the spins.[22]

Finally, the donor-electron magnetic moment is regarded as being in a thermal equilibrium with the surrounding cloud of spins. This is an assumption made to simplify the problem and it should be valid for a large-polaron case (cf. the relevant discussion in Sec. II). However, at the present moment an appropriate estimate of the relaxation times involved is not available.

The bound magnetic polaron (BMP) state discussed here can be interpreted as follows. The primary force supplying the localization of electron on a donor is the Coulomb attraction to the donor. The *s-d* coupling provides an additional potential well which increases the donor-electron binding energy. The local magnetization which gives rise to the additional potential may be decomposed into two parts. One of them is created by a molecular field produced by spin of the donor electron. The remaining part is supplied by a random alignment of the spins within the Bohr orbit of the donor and caused by a presence of thermodynamic fluctuations of magnetization. The role of the latter factor in the magnetic part of binding energy (Δ) can be decisive, as in the case of $Cd_{1-x}Mn_xSe$ at higher temperatures.

ACKNOWLEDGMENTS

The authors are grateful to Professor J. R. Anderson from the University of Maryland for a critical reading of the manuscript. This work was support-

ed in part by the Institute of Physics of the Polish Academy of Sciences through the project M.R.I.4.3.

APPENDIX A: FREE-ENERGY FUNCTIONAL FOR THE SPINS

We have included the *s-d* part in the donor-electron part. So, to avoid the double counting of this interaction, we consider here only the spin part of the Ginzburg-Landau functional, i.e., the part dependent only on local magnetization $\vec{M}(\vec{r})$

$$\mathscr{H}_s[\vec{M}(\vec{r})]=\int d^3r\, f[\vec{M}(\vec{r})]\ , \tag{A1}$$

where

$$f[\vec{M}(\vec{r})]=-\vec{M}(\vec{r})\cdot\vec{H}+\Phi[M(\vec{r})] +C[\nabla\vec{M}(\vec{r})]^2\ . \tag{A2}$$

We expand $f[\vec{M}(\vec{r})]$ around $\vec{M}_0$, at a given value of external field $\vec{H}$. We have

$$\vec{M}(\vec{r})=\vec{M}_0+\vec{\eta}(\vec{r})\ . \tag{A3}$$

Thus we have

$$f[\vec{M}(\vec{r})]=f[\vec{M}_0]+\vec{\eta}(\vec{r})\cdot\vec{\nabla}_{\vec{M}}f[\vec{M}]\,|_{\vec{M}_0} +\tfrac{1}{2}\sum_{i,j=1}^{3}\eta_i(\vec{r})\eta_j(\vec{r})\frac{\partial^2 f[\vec{M}]}{\partial M_i\partial M_j}\bigg|_{\vec{M}_0}+\cdots\ . \tag{A4}$$

Noting that

$$\nabla_{\vec{M}}f[\vec{M}]\,|_{\vec{M}_0}=0\ ,$$

we get

$$F_s[\vec{M}(\vec{r})]\equiv-\vec{M}(\vec{r})\cdot\vec{H}+\Phi[M(\vec{r})] =F_s[\vec{M}_0]+{\sum_{i,j}}'\frac{\eta_i\eta_j}{2}\frac{\partial^2F_s[\vec{M}]}{\partial M_i\partial M_j}\bigg|_{\vec{M}_0}+\cdots\ ,$$

or, since $\partial^2F_s\,|\,\partial M_i\partial M_j=0$ for $i\neq j$,

$$F_s[\vec{M}(\vec{r})]=F_s[\vec{M}_0]+\frac{1}{2}\left[\frac{\eta_\perp^2}{\chi_\perp(T,H)}+\frac{\eta_{||}^2}{\chi_{||}(T,H)}\right]+\cdots\ , \tag{A5}$$

where

$$\chi_\perp(T,H)=\frac{\partial^2F_s}{\partial M_x^2}\bigg|_{\vec{M}_0}=\frac{\partial^2F_s}{\partial M_y^2}\bigg|_{\vec{M}_0} \tag{A6}$$

and

$$\chi_{||}(T,H)=\frac{\partial^2F_s}{\partial M_z^2}\bigg|_{\vec{M}_0}\ . \tag{A7}$$

Now we will find an explicit expression for $\chi_{||}$ and $\chi_\perp$. Assume that volume of the system is $V=1$. Then

$$\frac{\partial F_s}{\partial M_z}\bigg|_{\vec{M}_0}=-H+\frac{\partial\Phi}{\partial M}\frac{\partial M}{\partial M_z}\bigg|_{\vec{M}_0}=0\ . \tag{A8}$$

Thus

$$\frac{\partial\Phi}{\partial M}\bigg|_{\vec{M}_0}=H\ ,$$

since

$$\frac{\partial M}{\partial M_z}\bigg|_{\vec{M}_0}=1\ .$$

Additionally,

$$\frac{\partial^2F_s}{\partial M_z^2}\bigg|_{\vec{M}_0}=\frac{\partial^2\Phi}{\partial M^2}\bigg|_{\vec{M}_0}\left[\frac{\partial M}{\partial M_z}\right]^2\bigg|_{\vec{M}_0} +\frac{\partial\Phi}{\partial\vec{M}}\bigg|_{\vec{M}_0}\frac{\partial^2M}{\partial M_z^2}\bigg|_{\vec{M}_0}\ . \tag{A9}$$

Hence

$$\frac{\partial^2F_s}{\partial M_z^2}\bigg|_{\vec{M}_0}=\frac{\partial^2\Phi}{\partial M^2}\bigg|_{\vec{M}_0}\equiv\frac{1}{\chi_{||}(T,H)}\ . \tag{A10}$$

Analogically,

$$\frac{\partial F_s}{\partial M_x}=-H\frac{\partial M_z}{\partial M_x}+\frac{\partial\Phi}{\partial M}\frac{\partial M}{\partial M_x} =\frac{\partial\Phi}{\partial M}\frac{\partial M}{\partial M_x}\ , \tag{A11}$$

and

$$\frac{\partial^2F_s}{\partial M_x^2}\bigg|_{\vec{M}_0}=\frac{\partial^2\Phi}{\partial M^2}\bigg|_{\vec{M}_0}\left[\frac{\partial M}{\partial M_x}\right]^2\bigg|_{\vec{M}_0} +\frac{\partial\Phi}{\partial M}\bigg|_{\vec{M}_0}\frac{\partial^2M}{\partial M_x^2}\bigg|_{\vec{M}_0}\ . \tag{A12}$$

But

$$\frac{\partial M}{\partial M_x}\bigg|_{\vec{M}_0}=0,\quad\frac{\partial^2M}{\partial M_x^2}\bigg|_{\vec{M}_0}=\frac{1}{M_0(T,H)}\ . \tag{A13}$$

So, finally

$$\left.\frac{\partial^2 F_s}{\partial M_x^2}\right|_{\vec{M}_0}=\frac{H}{M_0(T,H)}\equiv\frac{1}{\chi_\perp(T,H)}\ . \tag{A14}$$

It still remains to prove that $\chi_{||}(T,H)$ defined through (A10) is identical to the isothermal longitudinal susceptibility defined as the second derivative of free energy.

$$\chi_{||}=-\left.\frac{\partial^2 F_s}{\partial H^2}\right|_{\vec{M}_0}\ . \tag{A15}$$

For this we calculate

$$\frac{\partial F_s}{\partial H}=-M_z-H\frac{\partial M_z}{\partial H}+\frac{\partial\Phi}{\partial M}\frac{\partial M}{\partial H} \tag{A16}$$

and

$$\begin{aligned}\left.\frac{\partial^2 F_s}{\partial H^2}\right|_{\vec{M}_0}=&\chi_{||}-H\left.\frac{\partial^2 M_z}{\partial H^2}\right|_{\vec{M}_0}-\left.\frac{\partial M_z}{\partial H}\right|_{\vec{M}_0}\\&+\left.\frac{\partial^2\Phi}{\partial M^2}\right|_{\vec{M}_0}\left[\left.\frac{\partial M}{\partial H}\right|_{\vec{M}_0}\right]^2\\&+\left.\frac{\partial\Phi}{\partial M}\right|_{\vec{M}_0}\left.\frac{\partial^2 M}{\partial H^2}\right|_{\vec{M}_0},\end{aligned} \tag{A17}$$

and since

$$\left.\frac{\partial M}{\partial H}\right|_{\vec{M}_0}=\left.\frac{\partial M}{\partial M_z}\right|_{\vec{M}_0}\left.\frac{\partial M_z}{\partial H}\right|_{\vec{M}_0}=\chi_{||}\ ,$$

we have

$$\frac{1}{\chi_{||}}=\left.\frac{\partial^2\Phi}{\partial M^2}\right|_{\vec{M}_0}=\frac{1}{\chi_{||}(T,H)}\ , \tag{A18}$$

which provides the desired relation. It should be pointed out here that our expansion (A4) or (A5) is also valid for a magnetic phase provided $|\vec{\eta}|\ll|\vec{M}_0|$, i.e., beyond the critical region or for sufficiently strong fields.

APPENDIX B: PROBABILITY DISTRIBUTION IN GENERAL CASE

Applied magnetic field $\vec{H}$ is creating an axial anisotropy of various quantities even though the medium by itself is isotropic when the field is absent. In this appendix we consider an influence of this anisotropy on the effective Hamiltonian $\mathscr{H}(\vec{\Delta})$. The full form of $\mathscr{H}(\vec{\Delta})$ is

$$\begin{aligned}\mathscr{H}(\vec{\Delta})=&\frac{\hbar^2}{2m^*a^2}-\frac{e^2}{\kappa a}-k_BT\ln\left[2\cosh\left[\frac{\Delta}{2k_BT}\right]\right]\\&+\frac{4\pi a^3}{\chi_{||}(T,H)}\left[\frac{g\mu_B}{\alpha}\right]^2(\vec{\Delta}-\vec{\Delta}_0)^2\\&+4\pi a^3\left[\frac{g\mu_B}{\alpha}\right]^2\vec{\Delta}_\perp^{\,2}\left[\frac{1}{\chi_\perp(T,H)}-\frac{1}{\chi_{||}(T,H)}\right]\end{aligned} \tag{B1}$$

We get the previous form (3.16) assuming that $\chi_\perp=\chi_{||}$. The form (B1) leads to the probability distribution corresponding to (3.25) then

$$\begin{aligned}P(\Delta)=&\text{const}\Delta^2\cosh\left[\frac{\Delta}{2k_BT}\right]\exp\left[-\frac{4\pi a^3}{\chi_{||}}\left[\frac{g\mu_B}{\alpha}\right]^2\frac{\Delta^2}{k_BT}\right]\\&\times\int_{-1}^{1}dx\exp\left[\left[\frac{g\mu_B}{\alpha}\right]^2\frac{\Delta\Delta_0}{k_BT}4\pi a^3\left[\frac{2x}{\chi_{||}}-\frac{\Delta}{\Delta_0}(1-x^2)\frac{\chi_{||}-\chi_\perp}{\chi_\perp\chi_{||}}\right]\right],\end{aligned} \tag{B2}$$

where const contains all terms independent of Δ. So, the probability distribution of spin splitting Δ is given by the error function.

APPENDIX C: DERIVATION OF THE EFFECTIVE HAMILTONIAN $\mathscr{H}(\Delta)$

The effective Hamiltonian (3.2) is composed of two parts: the donor-electron part

$$\mathscr{H}_c=-k_BT\ln\left[2\cosh\left[\frac{\Delta}{2k_BT}\right]\right]+E_D(a) \tag{C1}$$

and the spin part

$$\mathscr{H}_s(\Delta)=\int_{-\infty}^{\infty}\prod_{\vec{q}}{}' d^3\eta'_{\vec{q}}d^3\eta''_{\vec{q}}\exp\left[-\frac{\mathscr{H}_s\{\vec{\eta}_{\vec{q}}\}}{k_BT}\right]\delta\left[\vec{\Delta}-\vec{\Delta}_0-\frac{2\alpha}{g\mu_B}\sum_{\vec{q}}{}'\mathrm{Re}(\vec{\eta}_{\vec{q}}b^*_{\vec{q}})\right]. \tag{C2}$$

In what follows we evaluate the integrals involved in (C2) analytically. The first step is to integrate over one of the variables, i.e., $\vec{\eta}'_{\vec{q}_0}$.

We introduce the notation $\vec{\Delta}=\{\Delta_i\}$, $\vec{\Delta}_0=\{\Delta_{0i}\}$, and

$$\lambda_i=\frac{g\mu_B(\Delta_i-\Delta_{0i})}{2\alpha}. \tag{C3}$$

After integration we get

$$\mathscr{H}_s(\vec{\Delta})=-k_BT\ln\left[\int_{-\infty}^{\infty}\prod_{\vec{q}}{}'' d^3\eta'_{\vec{q}}\,d^3\eta''_{\vec{q}}\right.$$

$$\left.\times\prod_{i=1}^{3}\exp\left\{-\beta\left[\sum_{\vec{q}}{}''\chi_i^{-1}(\vec{q})(\eta'^2_{i\vec{q}}+\eta''^2_{i\vec{q}})+\chi^{-1}_{\vec{q}_0}b^{-2}_{\vec{q}_0}\left[\lambda_i-\mathrm{Re}\sum_{\vec{q}}{}''\eta_{i\vec{q}}\,b^*_{\vec{q}}\right]^2\right]\right\}\right]-3k_BT\ln\frac{g\mu_B}{2\alpha b_{\vec{q}_0}}, \tag{C4}$$

where $\prod''_{\vec{q}}$ and $\sum''_{\vec{q}}$ mean that the factor and term containing $\eta'_{\vec{q}_0}$ are omitted. Additionally,

$$\chi_i=\begin{cases}\chi_{\parallel} & \text{for } i=3\\ \chi_{\perp} & \text{for } i=1,2\end{cases}. \tag{C5}$$

We rewrite the numerator of the exponential function contained in (C4) for each component i in the form

$$f\{\eta_j\}=\sum_j\chi_j^{-1}\eta_j^2+\chi^{-1}_{\vec{q}_0}b^{-2}_{\vec{q}_0}\left[\lambda-\sum_j\eta_jb_j\right]^2, \tag{C6}$$

where the new variable j runs over $(N-1)$ points $\vec{q}\neq\vec{q}_0$ in the first Brillouin zone. The quadratic form (C6) can be transformed to a form which does not include the linear terms by $\eta_j=y_j+a_j$, where

$$a_j=\frac{\chi_jb_j\lambda}{b^2_{\vec{q}_0}\chi_{\vec{q}_0}+\sum_j b_j^2\chi_j}. \tag{C7}$$

We get then

$$f\{y_j\}=\sum_j\chi_j^{-1}y_j^2+\chi^{-1}_{\vec{q}_0}b^2_{\vec{q}_0}\left[\sum_j b_jy_j\right]^2+\lambda^2\left[b^2_{\vec{q}_0}\chi_{\vec{q}_0}+\sum_j b_j^2\chi_j\right]^{-1}. \tag{C8}$$

The first two terms in (C8) give, after integration over y_j, an irrelevant constant in $\mathscr{H}_s(\vec{\Delta})$ so we disregard them. The last term is a constant in the integration procedure and it contains the information relevant for us since $\lambda=\lambda(\vec{\Delta})$. Therefore, finally

$$\mathscr{H}_s(\vec{\Delta})=\frac{\vec{\Delta}_{\perp}^2}{8\epsilon_{p\perp}}+\frac{(\vec{\Delta}_{\parallel}-\vec{\Delta}_0)^2}{8\epsilon_{p\parallel}}, \tag{C9}$$

where $\epsilon_{p\perp,\parallel}$ is given by (3.15). Hence adding up (C1) and (C9) we get the effective Hamiltonian represented by Eq. (3.14).

APPENDIX D: MATERIAL PARAMETERS OF $Cd_{1-x}Mn_xSe$

The theory presented in this paper contains the following parameters: the field-induced magnetization for the spins $M_0(T,H)$, the Lande factors for spins (g) and the donor electron (g^*), the effective mass of electron at the bottom edge of the conduction (Γ_7) band m^*, and the static dielectric constant κ. In the temperature range 1.5–2.4 K and up to field $H=60$ kOe, the field dependence of magnetization can be parametrized by the Brillouin function[9,23]

$$M_0(T,H)=\tfrac{5}{2}g\mu_B\bar{x}N_0B_{5/2}[g\mu_BH/k_B(T+T_0)], \tag{D1}$$

with $g=2$, and $N_0=n_0/V_0$ is the number of cations per unit volume. The quantities $\bar{x}$ and T_0 are [T. Dietl, M. Otto, H. Pawlowska (unpublished), and Ref. 23] $\bar{x}=0.027$, 0.041; $T_0=1.2$, 2.15 K for the concentration of magnetic (Mn^{2+}) ions $x=0.05$ and 0.1, respectively. The other quantities are[24] $g^*=0.52$, $m^*/m_0=0.13$, and $\kappa=9.4$, which gives $a_B=38$ Å. For the sake of simplicity we assume that the magnetization $M_0(T,H)$ is described by Eq. (D1) up to $T=10$ K. This underestimates the measured value of M_0 ($T=10$ K, H) by 10%.

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