as in the case of multiple trapping, the mechanism for transport cannot be uniquely determined from transit-time experiments.

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Effect of Fluctuations of Magnetization on the Bound Magnetic Polaron: Comparison with Experiment

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Thermal properties of large magnetic polarons localized on donors in a magnetic semiconductor are studied theoretically with the effect of thermodynamic fluctuations of magnetization taken into account. The model quantitatively describes recent spin-flip Raman scattering data for $Cd_{0.95}Mn_{0.05}Se$.

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In order to explain strong anomalies in the electrical conductivity of magnetic semiconductors,[1] and in the optical properties[2,3] of semimagnetic semiconductors,[4] the concept of the bound magnetic polaron (BMP) has been proposed.[2,3,5] The BMP consists of an impurity electron in the localized state, which induces by the s-d interaction a space-inhomogeneous local magnetization in its neighborhood. This magnetization, in turn, leads to the spin splitting of the impurity level, even in the absence of an external magnetic field.

Existing theories[2,5,6] of BMP are based on the mean-field approach (MFA). Their starting point is usually the Ginzburg-Landau free energy functional with two variational parameters: magnetization density $\vec{\eta}(\vec{r})$ due to presence of the impurity electron, and the effective Bohr radius a of the impurity-electron wave function $\varphi(\vec{r})$. Detailed calculations predict a type of critical behavior similar to that for a bulk ferromagnet in MFA: a critical temperature T_P through a divergence of static susceptibility χ, and a square-root dependence of $\vec{\eta}(\vec{r})$ and of the electron spin splitting on $T_P - T$.

These results, as we show in the following, are in direct conflict with recent experimental results for $Cd_{0.95}Mn_{0.05}Se$. In particular, the critical behavior in χ is absent, and the zero-field spin splitting persists above the mean-field value of T_P.

In this paper we demonstrate for the first time how the thermodynamic fluctuations influence the stability of BMP. The essentially new ingredient of our model is based on the observation that a degree of spin alignment around the donor

impurity may be caused not only by the molecular field produced by the impurity electron but also by the thermodynamic fluctuations of the magnetization. The influence of the latter factor can be relatively large because of the finite size of the system under consideration.

The theory presented here explains quantitatively the new spin-flip Raman scattering data of Nawrocki *et al.*,[3] concerning the measurement of the zero-field splitting, as well as its field dependence. Additionally, it provides a natural explanation of the absence of the critical behavior in χ, as expected for any system of a finite size.

We assume that we have $N_D V$ separated neutral donor centers. Electrons localized on the donors interact with localized spins $\{\vec{S}_i\}$ via contact s-d interaction, $-\alpha\sum\vec{S}_i\cdot\vec{s}_i$ where $\vec{s}_i$ is the spin operator for the electron located on ith Mn ion. The wave function $\varphi(\vec{r})$ of the donor electron is assumed to extend over many lattice sites, so that the spin fields of both the electron and the localized moments, $\vec{s}(\vec{r})$ and $\vec{S}(\vec{r})$, respectively, may be regarded as continuous functions of the relative distance r from the donor center. In addition, the electron wave function is taken as hydrogenic in form: $\varphi(\vec{r}) = (\pi a^3)^{-1/2}\exp(-r/a)$, where a is the effective Bohr radius, here regarded as a variational parameter. The form of $\varphi(\vec{r})$ implies that we limit ourselves to the regime of applied magnetic field in which the magnetic length $(c\hbar/eH)^{1/2}$ is larger than a, i.e., magnetic-field–induced ellipticity of $\varphi(\vec{r})$ may be neglected.

We utilize the rotationally invariant form of the molecular-field approach to the s-d interaction. Therefore, we can define the effective field due to this interaction acting on the electron spin and localized spin, respectively, as $\vec{H}^* = (\alpha/g^* g\mu_B{}^2)\vec{M}(\vec{r})$ and $\vec{H}_s = (\alpha/gg^*\mu_B{}^2)\vec{\gamma}$. Here g^* and g are the Landé factors of the electron and the spins, respectively: $\vec{M}(\vec{r}) = -g\mu_B\langle\vec{S}(\vec{r})\rangle$ is the magnetization due to spins, and $|\varphi(\vec{r})|^2\vec{\gamma} = -g^*\mu_B \times\langle\vec{s}(\vec{r})\rangle$, where $\vec{\gamma}$ is a vector pointing along the direction of the total magnetic field, given by $\int d^3r(\vec{H}^* + \vec{H})|\varphi|^2$, and describing the degree of electron polarization. Thus, the electron-spin splitting (energy of the spin flip) is given by

$$\Delta = g^*\mu_B\left|\int d^3r[\vec{H}^*(\vec{r}) + \vec{H}]\,|\varphi(\vec{r})|^2\right|. \tag{1}$$

Assuming further that the impurity electrons are in thermal equilibrium with the subsystem of magnetic ions, we can write down the Ginzburg-Landau (GL) functional per one donor in the form

$$F[\vec{M}(\vec{r})] = F_s[\vec{M}(\vec{r})] + \frac{\hbar^2}{2m^*a^2} - \frac{e^2}{\kappa a} - kT\ln\left\{2\cosh\frac{\Delta[\vec{M}(\vec{r})]}{2kT}\right\}. \tag{2}$$

The terms represent respectively the free energy of localized spins, the kinetic energy, the Coulomb energy, and the spin parts of the electron free energy.

The problem of finding the most probable spin configuration is simplified considerably when we note the following. The spin cloud surrounding the localized electron is of finite size but large enough to be treated as a classical subsystem undergoing thermodynamic fluctuations. Since only the fluctuations within effective radius a around the donor are relevant to us, we assume that the fluctuating part of the magnetization scales with the probability of finding the electron, $|\varphi(\vec{r})|^2$. Then the local magnetization around the donor takes the form $\vec{M}(\vec{r}) = \vec{M}_0 + \vec{\eta}\exp(-2r/a)$, where $\vec{M}_0$ is the response to an external field $\vec{H}$, and $\vec{\eta}$ is a parameter to be determined from the variational approach. The form of $\vec{M}(\vec{r})$ given above also reproduces correctly the linear response of the spins to field $\vec{H}_s(\vec{r})$.

To proceed further we insert $\vec{M}(\vec{r})$ into the free energy (2), and expand $F_s[\vec{M}(\vec{r})]$ around $\vec{M}_0$. We drop the term $\sim\nabla\cdot\vec{M}(\vec{r})$ in the expansion since we are considering here the paramagnetic case only. Assuming further that $\vec{\eta}$ is small compared to the saturation value of $\vec{M}_0(\vec{H})$, we arrive at

$$F_s[\vec{M}(\vec{r})] = F_s(\vec{M}_0) + \vec{\eta}^2\pi a^3/16\chi(T,H), \tag{3}$$

where $\chi(T,H) = \partial M_0/\partial H$. The accuracy of (3) can be estimated by noting that corrections to this equation coming from the higher-order contributions for the most probable value of $\eta = \bar{\eta}$ are of the order $\bar{\eta}^2/M_s$. Strictly speaking, in (3) we have omitted the difference between longitudinal ($\chi = \chi_\parallel$) and transverse ($\chi_\perp$) parts of the static susceptibility for given $H \neq 0$. This leads to an additional term $\sim(1/\chi_\parallel - 1/\chi_\perp)\eta_\perp{}^2$. This is negligible for both weak and strong fields, and will be neglected in the following.

We introduce the vector $\vec{\Delta} = \alpha(\vec{M}_0 + \frac{1}{8}\vec{\eta})/g\mu_B + g^*\mu_B\vec{H}$, and define the effective Hamiltonian of the system as $\mathcal{H}(\vec{\Delta}) = F[\vec{M}(\vec{r})] - F_s(\vec{M}_0)$.

Firstly, we summarize the main mean-field results. In this approach one identifies the most probable value $\bar{\Delta}$ of spin splitting Δ with

the one minimizing $\mathcal{H}(\vec{\Delta})$. One gets

$$\bar{\Delta} - 2\epsilon_p \tanh(\bar{\Delta}/2kT) - \Delta_0 = 0, \quad (4)$$

with

$$\epsilon_p(T,H) = \alpha^2\chi(T,H)/32\pi g^2\mu_B{}^2a^3$$

and $\Delta_0 = (\alpha/g\mu_B)M_0 + g^*\mu_B H$. At low temperature or in magnetic field, $\bar{\Delta}/kT \gg 1$, and then $\bar{\Delta} = 2\epsilon_p + \Delta_0$. For $H = 0$ and $kT \to \epsilon_p$ one gets classical critical behavior for $\bar{\Delta}$ (and thus for $\bar{\eta}$).

The effective Bohr radius $a = a_B$ can be found by minimizing ΔF, where ΔF is the contribution to the free energy due to the presence of the donor [in MFA, $\Delta F = \mathcal{H}(\vec{\Delta})$]. The total susceptibility is $\chi_t = \chi - N_D\partial^2\Delta F/\partial H^2$, and shows ordinary critical behavior for $kT \to \epsilon_p$.

However, at nonzero temperature the region of parameters beyond the minimum of $\mathcal{H}(\vec{\Delta})$ is also accessible to the system. The probability distribution governing such fluctuations is $P(\vec{\Delta}) = C\exp[-\mathcal{H}(\vec{\Delta})/kT]$, with C a normalizing constant. Integrating $P(\vec{\Delta})$ over angles we obtain the probability of spin splitting Δ, $P(\Delta)$. The key suggestion of our work is that $P(\Delta)$, possibly slightly broadened by fluctuations of composition, describes the observed line shape in the spin-flip Raman scattering experiments.[3] In particular, the position of the line corresponds to the maximum of $P(\Delta)$. This peak position is therefore given by $\bar{\Delta}$ determined from $dP(\Delta)/d\Delta|_{\Delta=\bar{\Delta}} = 0$. Thus we get

$$\bar{\Delta}^2 - 2\epsilon_p\bar{\Delta}\tanh\left(\frac{\bar{\Delta}}{2kT}\right) - \bar{\Delta}\Delta_0\coth\left(\frac{\bar{\Delta}\Delta_0}{4\epsilon_p kT}\right) - 4\epsilon_p kT = 0. \quad (5)$$

At low temperatures or in high fields we recover the mean-field result (4). This is because at low temperatures fluctuations are absent, while in high fields the quantization axis is fixed by $\vec{M}_0$, and thus the effect of fluctuations averages to zero. On the other hand, contrary to the mean-field expectations, for $H = 0$ and in the regime of high temperatures $kT \gg \epsilon_p$, the spin splitting still persists. According to (5) it is given then by $\Delta = (8\epsilon_p kT)^{1/2}$. This spin splitting is caused entirely by the thermodynamic fluctuations, as can be seen from the following argument, based solely on the idea of fluctuating paramagnetic blocks.

Divide the crystal into blocks of volume L^3, where $\xi \ll L \ll a$ (ξ is the magnetic coherence length). The spin splitting on average is given by summing up over blocks $\{i\}$ [cf. Eq. (1)],

$$\Delta = (\alpha L^3/g\mu_B)\left|\textstyle\sum_i \vec{M}_i\,|\,\varphi(\vec{r}_i)\right|^2. \quad (6)$$

Since $\langle\vec{M}_i\cdot\vec{M}_j\rangle = (2kT/L^3)\chi\delta_{ij}$, replacing summation with the integration, we get Δ, which coincides with the previous value for $kT \gg \epsilon_p$.

Finally, we calculate ΔF, which includes the fluctuations.[7] We find

$$\Delta F = \frac{\hbar^2}{2m^*a^2} - \frac{e^2}{\kappa a} - \frac{\epsilon_p}{2} - kT\ln\left[2\cosh\left(\frac{\Delta_0}{2kT}\right) + \frac{4\epsilon_p}{\Delta_0}\sinh\left(\frac{\Delta_0}{2kT}\right)\right]. \quad (7)$$

Again, the effective Bohr radius is determined from the minimalization of ΔF. Also, the magnetic susceptibility at $H = 0$ is now

$$\chi_t = \chi + \frac{N_D\mu_B{}^2}{4kT}\left(\frac{\alpha\chi}{g\mu_B{}^2} + g^*\right)^2\left(1 + \frac{\epsilon_p}{3kT}\right)\left(1 + \frac{\epsilon_p}{kT}\right)^{-1}. \quad (8)$$

Hence, the critical behavior is washed out by the fluctuations (cf. Fig. 1).

Now, we compare our results with the experimental data for $Cd_{0.95}Mn_{0.05}Se$. The theory contains the following parameters: $M_0(T,H)$, g, g^*, m^*, and κ. We take $M_0(T,H)$ from our own measurements of χ presented in Fig. 1 (in the low-field region), as well as from the high-field measurements.[8] In the temperature range 1.5–4.2 K and up to 60 kOe, $M_0(T,H)$ can be parametrized by the Brillouin function $M_0(T,H) = g\mu_B \times N_0 B_{5/2}(g\mu_B H/k(T+T_0))$, with $g = 2$, $x = 0.027$, $T_0 = 1.2$ K, and N_0 being the number of cations per unit volume.

Detailed studies[9] of transport properties of $Cd_{0.95}Mn_{0.05}Se$ show that the donor ionization energy is close to the value for CdSe,[10] $E_D = (20 \pm 1)$ meV, which gives $a_B \simeq 38$ Å. Thus we take[10] $g^* = 0.52$, $m^*/m_0 = 0.13$, and $\kappa = 9.4$, i.e., the observed values for CdSe. There are about 200 Mn ions within volume $\frac{4}{3}\pi a_B{}^3$.

We determine the s-d exchange constant α by fitting $\Delta(H)$ in high fields (cf. Fig. 2). We obtain from this fitting $\alpha N_0 = 280 \pm 30$ meV, where the error corresponds to the uncertainty of the data

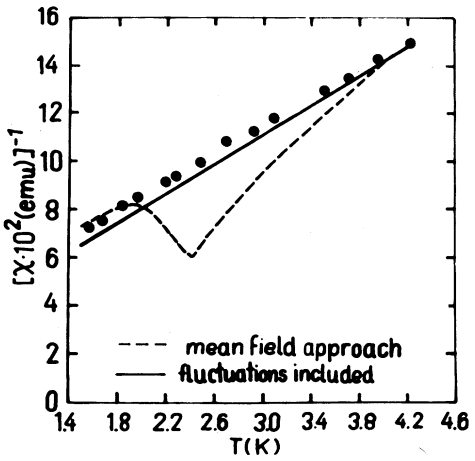

FIG. 1. Temperature dependence of inverse susceptibility of $Cd_{0.95}Mn_{0.05}Se$ in field 40 Oe. Dots, experiment; solid line, theory with fluctuations included; dashed line, MFA. Donor concentration is 1.2×10^{17} cm^{-3}.

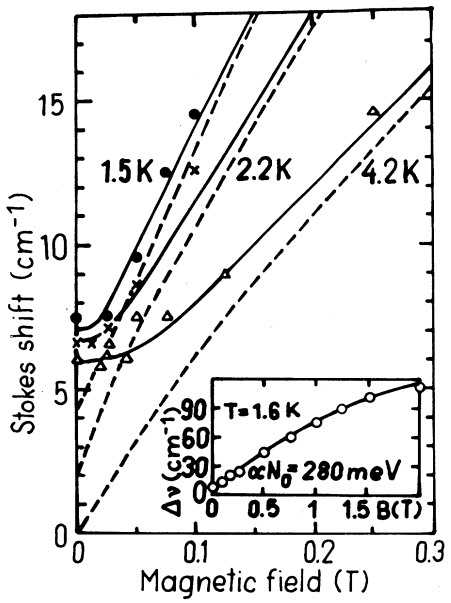

FIG. 2. The Stokes shift of the Raman scattering line in low fields at various temperatures, and in high fields at 1.6 K (inset). Experimental points, after Ref. 3. Solid lines, theory including fluctuations. Dashed lines, MFA.

for $M_0(H, T)$. Taking the material parameters we get the MFA critical temperature, $T_p \simeq 2.5$ K. In Fig. 2 we compare our results with the spin-splitting of the donor level measured by Nawrocki *et al.*[3] It is clear that the agreement between the theory and experiment can be reached only after including the thermodynamic fluctuations.

Finally, we would like to interpret our data by stating the difference between the concepts of BMP discussed before[5] and the one invoked here. The shortest definition of BMP is as follows: Because of the s-d coupling a carrier digs out a potential well aligning the surrounding spins, and localizes itself in it. The electrostatic attraction to a donor plays a role of an additional factor, which strongly favors such localization. On the other hand, we show that the electron further lowers its energy as it aligns its spin with the local magnetization created by the thermodynamic fluctuations. The resultant picture given here combines those two effects.

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