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Magnetic polaron: Theory and experiment

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We present a general thermodynamic model of the bound magnetic polaron which takes into account the free energies of the localized spins, of the free carriers, of the electrons localized in the bound magnetic polarons, and of the electrons trapped on impurities which play the role of compensators. In addition to the configurational entropy, a magnetic entropy is associated with the bound magnetic polarons. It is shown that this magnetic entropy characterizes the bound magnetic polaron, and most physical properties are closely related to its order of magnitude. In particular, it is shown that this entropy is responsible for the stability of the bound magnetic polaron at high temperature both in EuO and in semimagnetic semiconductors such as $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$. Our model accounts well for the physical properties of these materials. The extension of the model to other magnetic semiconductors is also discussed.

I. INTRODUCTION

The concept of magnetic polarons was introduced by de Gennes[1] and then has been studied by several authors[2] many years ago. The further developments of this concept[3] were motivated essentially to explain the outstanding metal-insulator transition in Eu-rich EuO at $T \sim 50$ K evidenced by Oliver *et al.*[4] below the Curie temperature $T_C \sim 69$ K. The basic idea is that the outer electron of the oxygen vacancy can be trapped by the vacancy which acts as a donor, and polarizes the localized spins of Eu surrounding the vacancy, through the *d-f* exchange interaction. This is the picture of the bound magnetic polaron. Simultaneously, Torrance *et al.*[5] and Leroux Hugon[6] proposed that this transition is due to an overlap of magnetic polarons depending on the temperature and on the concentration of oxygen vacancies. The description in Ref. 5, however, is purely qualitative. Leroux Hugon has calculated the Mott instability of such a polaron and claimed that his model could account for the metal-insulator transition observed at 50 K for the particular concentration of oxygen vacancies $n \simeq 4\times 10^{19}$ cm^{-3}.[4] However, this agreement is an artifact, essentially due to a too large value of the effective mass of the conduction electrons used in the numerical calculations. In fact, with a realistic choice of the parameters entering this model, the results are in complete disagreement with experiment, and do not depart significantly from the usual Mott criterion for calculating the critical carrier density for the formation of bound hydrogenic impurity states independent of temperature. The reasons of the failure of this model will be discussed later in this paper. Nagaev and Grigin[7] have calculated the response of a free-carrier electron gas polarized by exchange interactions when it is submitted to an electric perturbation. However, this calculation is made in a spin-wave approximation and its range of validity is then restricted to low temperatures. The first consistent model of bound magnetic polarons is the beautiful work of Kübler and Vigren[8] and consists of the calculation of a self-consistent magnetically controlled electron localization in the random-phase approximation. This model accounts for the main features of the experimental properties of EuO in the ferromagnetic configuration, in particular the strong temperature dependence of the vacancy concentration at which a metal-insulator transition occurs.

However, all these models together with subsequent ones[9–11] are in strong disagreement with experiment in the paramagnetic configuration. In particular, these models predict that EuO is metallic at room temperature as soon as the concentration of oxygen vacancies n exceeds few 10^{18} cm^{-3}, contrary to experiments showing that EuO is insulating up to $n \sim 10^{20}$ cm^{-3}.[12] We have shown in Ref. 13 that such a discrepancy is essentially due to the fact that these models neglect the magnetic entropy associated with the formation of a bound magnetic polaron, and that this entropy lowers the free energy of the magnetic polaron. This concept has also been used by Dietl and Spalek[14] to explain physical properties due to the presence of bound magnetic polarons in $Cd_{1-x}Mn_xSe$. This material is a *semi*magnetic material since the number of localized spins per unit cell is $x \ll 1$, in contrast to magnetic semiconductors like EuO where $x \sim 1$. In fact, the description of the magnetic polaron in semimagnetic semiconductors is much simpler than in magnetic semiconductors because the magnetic interactions are much smaller due to the large distance between the localized spins. It follows that in semimagnetic semiconductors the free energy can be linearized in terms of the magnetic energy and entropy of the polaron, with all the simplifications inherent to the perturbation methods.

Our purpose in this paper is to develop our model outlined in Ref. 13, based on a thermodynamic calculation of the free energy of the system. Although the model is quite general, we shall develop it with the application to EuO in mind because it is the only magnetic semiconductor where magnetic polarons are evidenced without any ambiguity, and because the description of the magnetic polaron in such a material presents the highest complexity. Then it will be easy to show that the model of bound magnetic polaron in semimagnetic semiconductors, as developed in Ref. 14, is in fact a particular case of our previous model[13] including further approximations which will be discussed. The limit of our model and its use to get a better understanding of the metal-insulator transitions in other rare-earth compounds are also analyzed.

II. THERMODYNAMIC MODEL

The free energy of the statistical system is the sum of various contributions from the free-electron gas, from the localized spins S ($S=\frac{7}{2}$ for Eu^{2+} in EuO and $S=\frac{5}{2}$ for Mn^{2+} in $Cd_{1-x}Mn_xSe$), from the bound magnetic polarons, from the impurities, and in rare-earth compounds we shall see that the contribution from the $4f$ levels must also be taken into account. Our purpose in this paragraph is to calculate separately all these various contributions. To simplify the notations all the free energies will be expressed per unit cell, i.e., per unit volume $(a')^3/4$ where a' is the lattice parameter of the fcc lattice.

A. Free energy of the localized spin system

In the absence of free carriers, the localized spins are coupled by a direct exchange interaction described by the Heisenberg Hamiltonian

$$H_0=-\frac{1}{2}\sum_{i,j} I(R_{ij})\vec{S}_i\vec{S}_j \ . \tag{2.1}$$

In the presence of free carriers, the localized spins S_i are also coupled to the spin density $\vec{s}(r)$ of the carriers. We shall write this indirect exchange interaction as

$$H_1=-\sum_n J\vec{S}_n\cdot\vec{s}(R_n) \ . \tag{2.2}$$

The first order of approximation in a perturbation expansion of this Hamiltonian gives the energy of the free carriers,

$$E(k)^{\pm}=E^0(k)\pm\frac{1}{2}JS\sigma \ , \tag{2.3}$$

where σ is the polarization of the localized spins: $\sigma=|\langle\vec{S}\rangle|/S|$. $E^0(k)$ is the energy of the carriers before the introduction of the exchange interaction. The signs + and − refer to polarizations ↓ and ↑ of the spin of the carriers, respectively. The second-order terms provide the indirect exchange interaction

$$H_{ex}=-\frac{1}{2}\sum_{i,j} J_{eff}(R_{ij})\vec{S}_i\vec{S}_j \ , \tag{2.4}$$

where the effective exchange constant J_{eff} can be written[15,16]

$$J_{eff}(R_{ij})=\left[\frac{J}{2N_0}\right]^2\sum_q \chi_0^+(q)e^{i\vec{q}\cdot\vec{R}_{ij}} \ , \tag{2.5}$$

where N_0 is the number of localized spins, and

$$\chi_0^+(q)=\chi_{0\uparrow}(q)+\chi_{0\downarrow}(q) \tag{2.6}$$

is the free-electron-gas susceptibility. χ_{0s} is the Lindhart susceptibility function at zero ferquency,[17]

$$\chi_{0s}(q)=\sum_k \frac{n_{k+q,s}-n_{k,s}}{E^0(k)-E^0(k+q)} \ . \tag{2.7}$$

$n_{k,s}$ is the occupation number of the free carriers in the state of energy $E^0(k)$ with the spin s (↑ and ↓). The main approximations inherent to the model can be read in these expressions. First the free carriers are treated as s electrons.[17] This is a good approximation in Mn compounds where the conduction band is s or p type. In europium chalcogenides, however, the conduction band is essentially of a d type. In that case, it has been predicted by Nolting[18] that the down-spin spectrum should exhibit a multiband structure in which each up-spin band state splits in two. Recently, however, Allan and Edwards[19] have shown that in EuO and EuS no such splitting occurs, and that the corrections arising from the d character of the conduction band are in fact much smaller than predicted by Nolting: They have argued that there are no corrections for the majority up-spin states and only small shifts and broadening of the minority down-spin states due to electron-magnon interactions. We shall neglect such effects which are minor with respect to the large spin splitting between ↑ and ↓ states described by Eq. (2.3). Second, the free-electron susceptibility appears in Eq. (2.5) because we have neglected the correlation between the free carriers, which modifies the linear response of the electron gas. The susceptibility reads, in first approximation,[20]

$$\chi(q)=\chi_0^+(q)/[1-v\chi_0^+(q)] ,$$

where the potential v is usually repulsive. In principle, $\chi(q)$ should be substituted to $\chi_0^+(q)$ in Eq. (2.5). This effect may be important in metals, but for magnetic semiconductors, even heavily doped ones, the correction $v\chi_0^+(q)$ which is proportional to the density of states at the Fermi energy remains small and can be neglected. As a consequence, we shall neglect the electron-electron interaction, and evaluate $J_{\text{eff}}(R_{ij})$ from Eq. (2.5). This quantity has been calculated in Ref. 15 as follows:

$$J_{\text{eff}}(R_{ij})=-\frac{2}{W}\left[\frac{VJ}{2\pi^2N_0R_{ij}}\right]^2\left[\sum_{m=-\infty}^{+\infty}(-1)^m\left[\frac{\sin(\pi R_{ij}/a)}{(R_{ij}+ma)^2}-\frac{\pi}{a}\frac{\cos(\pi R_{ij}/a)}{R_{ij}+ma}\right]\right.$$
$$\left.\times\int_0^{\pi/a}\{f[E^+(k)]+f[E^-(k)]\}\frac{k\sin(kR_{ij})\sin(mka)}{\sin ka}\right] . \tag{2.8}$$

W is the bandwidth of the free-carrier states, N_0 is the number of localized spins in the volume V, $f(E)$ is the Fermi distribution, and the length a is related to the lattice parameter a' according to the relation

$$a=\left[\frac{\pi}{3}\right]^{1/3}\frac{a'}{2} . \tag{2.9}$$

In a molecular-field approximation the assembly of localized spins interacting via the direct and indirect exchange can be replaced by a system of noninteracting spins in an effective magnetic field,

$$H=\frac{\sigma s}{g\mu_B}J_0+H_{\text{ext}} , \tag{2.10}$$

where g is the Lande factor, μ_B is the Bohr magneton, and J_0 is the Fourier transform of the total exchange constant $J_{\vec{k}}$ at $k=0$ defined by

$$J_{\vec{k}}=\sum_i[I(\vec{R}_{ij})+J_{\text{eff}}(\vec{R}_{ij})]e^{i\vec{k}\cdot\vec{R}_{ij}} . \tag{2.11}$$

An additional external field H_{ext} has been included for completeness. Then the particular function of the localized-spin assembly in the canonical distribution is

$$Z=\left[\sum_{m=-S}^{+S}e^{g\mu_BmH/(k_BT)}\right]^{N_0} , \tag{2.12}$$

and the contribution $-k_BT\ln Z$ to the free energy is

$$F_M=x\left[\tfrac{1}{2}J_M(\sigma)S^2\sigma^2-k_BT\ln\left[\frac{\sinh[(2S+1)s\sigma J_M(\sigma)/(2k_BT)]}{\sinh[\sigma sJ_M(\sigma)/(2k_BJ)]}\right]\right] , \tag{2.13}$$

where k_B is the Boltzmann constant and x is the number of localized spins per unit cell ($x=1$ in europium chalcogenides and is smaller than 1 in semimagnetic semiconductors). The quantity $J_M(\sigma)$ defined by

$$J_M(\sigma)=I(0)+J_{\text{eff}}(0)+\frac{g\mu_BH_{\text{ext}}}{\sigma s} \tag{2.14}$$

depends on σ even when $H_{\text{ext}}=0$ below the Curie temperature, because $J_{\text{eff}}(0)$ depends on σ through the arguments of the Fermi function in Eq. (2.8). The polarization σ cannot be determined by the minimization of the free energy. The reason is that the spin system cannot be considered as mechanically isolated because the magnetic field H is a generalized force applied to the system.[21] Since σ is the "external parameter" associated with H, we can write

$$\sigma=-\left[\frac{\partial F_M}{\partial H}\right]\Big/(xg\mu_B) ,$$

which reads

$$\sigma=SB_S\left[\frac{\sigma^2J_0+g\mu_BSH_{\text{ext}}}{k_BT}\right] , \tag{2.15}$$

where B_S is the Brillouin function

$$B_S\{y\}=\frac{1}{2S}\left[(2S+1)\coth\frac{2Sy+y}{2S}-\coth\frac{y}{2S}\right] . \tag{2.16}$$

B. Free energy of the free-carrier gas

Since the metal-insulator transition is induced by the exchange of electrons between the polarons and the conduction band, the number of free carriers is not fixed *a priori*, and their free energy is best calculated from the particular function Θ in the grand-canonic distribution

$$\Theta=\prod_{\tau}\left[\sum_{n_\tau} e^{(E_F-\epsilon_\tau)n_\tau/(k_BT)}\right], \tag{2.17}$$

where n_τ is the number of electrons in the quantum state τ with the energy ϵ_τ. E_F is the Fermi energy (or the chemical potential of the free-carrier source). The free energy is given by

$$F_e=N_eE_F-k_BT\ln\Theta ,$$

and taking into account the fact that $n_\tau=0$ or 1 due to the Pauli principle, we get

$$F_e=N_eE_F-k_BT\int_0^\infty dE\,D(E)\ln(1+e^{(E_F-E)/(k_BT)}) , \tag{2.18}$$

where N_e is the number of carriers per unit cell,

$$N_e=\int_0^\infty dE\,D(E)(1+e^{(E-E_F)/(k_BT)})^{-1} . \tag{2.19}$$

$D(E)$ is the density of states in the conduction band, which according to Eq. (2.3), takes the form

$$D(E)=D^0(E+\tfrac{1}{2}JS\sigma)+D^0(E-\tfrac{1}{2}JS\sigma) . \tag{2.20}$$

$D^0(E)$ can be deduced from the dispersion relation of the free carriers,

$$E^0(k)=\frac{W}{2}(1-\cos ka') . \tag{2.21}$$

In fact Eq. (2.8) is derived with the lattice parameter a' replaced by the radius of the Wigner-Seitz cell a in Eq. (2.21). This ambiguity comes from the fact that this dispersion relation has been chosen isotropic for mathematical convenience, but is then too crude to describe the band structure of a crystal which has only the cubic symmetry. However, since the transport properties of the free carrier strongly depend on their effective mass m, we shall calculate the free energy of the free carriers with the relation (2.21) which gives the proper curvature of $E^0(k)$ at the bottom of the conduction band as deduced from optical data. We shall return to this point in the next section. In practice, the free-carrier concentration in the materials of interest is always small so that $k_Fa \ll 1$, where k_F is the wavelength at the Fermi level. In such a case, we can restrict the k-series expansion of Eq. (2.21) to the second order, in which case

$$D^0(E)=\frac{1}{2\pi^2}\frac{E^{1/2}}{W^{3/2}} . \tag{2.22}$$

Equations (2.18)–(2.22) determine F_e as a function of N_e, σ, and T.

C. Free energy of the bound magnetic polaron

As in the derivation of Eqs. (2.4)–(2.7), we shall make a static approximation which, here, consists in neglecting the time fluctuations of the electric field φ to which the electron is subjected, and then setting $\varphi(r)=e/r^3$. The effect of this field is to induce a redistribution of the electronic density $\delta\rho$ around the defect. We can write, in Fourier space,

$$\delta\rho_k=L_{11}(k)\varphi(k) . \tag{2.23}$$

From this equation, we can derive the dielectric function[22]

$$\epsilon(k)=\left[1-\frac{4\pi e^2}{\kappa_0k^2}L_{11}(k,\omega)\right]^{-1} , \tag{2.24}$$

where κ_0 is the dielectric constant. The peculiarity of the bound magnetic polaron is that the electric field φ also induces a redistribution of the spin density $\delta\vec{S}(\vec{r})$ due to the exchange coupling between the localized spin system and the electrons. According to Eq. (2.2) the density of exchange energy in the bound magnetic polaron is

$$E_{\text{ex}}=-\sum_n J[\vec{S}_n\delta(\vec{R}_n)+\delta\vec{S}_n(\vec{r}-\vec{R}_n)]\vec{s}(\vec{r}) , \tag{2.25}$$

where $\vec{s}(\vec{r})$ is the spin density of the bound electron. Let us take the electron wave function Ψ under the form

$$\Psi=(\pi R^3)^{-1/2}e^{-r/R} ,$$

where the Slater parameter R is a variational parameter. Then in terms of the Fourier transform of $|\Psi|^2$ equal to

$$(16/R^4)(k^2+4/R^2)^{-2} ,$$

the internal energy of one localized electron is

$$\mathscr{E}_\mp=\frac{\hbar^2}{2mR^2}-\frac{32e^2}{\pi R^4\kappa_0}\int_0^\infty\frac{d^3k}{\epsilon(k)(k^2+4/R^2)^2}\pm\frac{\Delta}{2} . \tag{2.26}$$

The two first terms are the kinetic energy and the Coulomb energy, respectively. The third term is the exchange energy, equal to E_{ex} integrated in the whole real space when Eq. (2.25) is treated in first order of perturbation,

$$\frac{\Delta}{2}=\frac{2J}{\pi^3R^4}\int_0^\infty \frac{S\sigma+\delta S^z_{\vec{k}}}{(k^2+4/R^2)^2}d^3k \ . \tag{2.27}$$

It represents the Fröhlich-Nabarro—term[23] analog to Eq. (2.3) for the free carrier. The − sign refers to the spin-up polarization of the bound electron and the + sign to the opposite case. $\delta S_{\vec{k}}$ is the Fourier transform of $\delta S(\vec{r})$. In Eq. (2.27), we have neglected the effect of the external magnetic field on Δ and assumed that $\delta\vec{S}$ was polarized along the z direction. These two approximations will be discussed later.

Formally, we can distinguish several contributions to the entropy $\mathscr{S}$ associated with the formation of the bound magnetic polaron. One contribution is a configurational entropy $\mathscr{S}_1$ resulting from the possibility for the bound electron to reverse its spin. The second one is the configurational entropy $\mathscr{S}_2$ associated with the various repartitions of n_d bound magnetic polarons among the N_d possible sites. Moreover, the excess of polarization $\delta S(\vec{r})$ not only modifies the internal energy [through the exchange term Δ in Eq. (2.26)] but also modifies the magnetic entropy by an amount $\mathscr{S}_3$ and both quantities Δ and $\mathscr{S}_3$ are first-order terms with the same order of magnitude. Then we can write the free energy in the form

$$\mathscr{F}_p=n_d\overline{\mathscr{E}}-T(\mathscr{S}_1+\mathscr{S}_2+\mathscr{S}_3) \ . \tag{2.28}$$

$\overline{\mathscr{E}}$ is the mean value of the internal energy in the canonical distribution deduced from Eq. (2.26). To make contact with other works, which we shall discuss later, we can also write $\mathscr{F}_p$ under the equivalent form

$$\mathscr{F}_p=\delta F^{(e)}+\delta F_M-T\mathscr{S}_2 \ , \tag{2.29}$$

where

$$\begin{aligned}&\delta F^{(e)}=n_d\overline{\mathscr{E}}-T\mathscr{S}_1 \ ,\\&\delta F_M=\delta^{(2)}E-T\mathscr{S}_3 \ .\end{aligned} \tag{2.30}$$

$\delta F^{(e)}$ is the electronic part of the free energy associated with the bound magnetic polaron. δF_M is the magnetic part. Therefore we can consider this term as the modification of the free energy F_M of the localized spins in Eq. (2.13) upon introduction of the nonuniform magnetization $g\mu_B\delta S(\vec{r})$. $\delta^{(2)}E$ is the modification of the exchange energy between the localized spin arising from the Hamiltonian (2.25) treated in the second order of perturbation, and has been introduced for completeness. However, this second-order term will be neglected with respect to $T\mathscr{S}_3$ and $\mathscr{E}$ which are first-order terms in magnetic semiconductors.

Let us now calculate $\mathscr{F}_p$ more explicitly. $\delta F^{(e)}$ can be derived as a whole from the partial partition function Z_p. We have

$$Z_p=\left[e^{-\mathscr{E}_+/k_BT}+e^{-\mathscr{E}_-/k_BT}\right]^{n_d} , \tag{2.31}$$

and we can then deduce

$$\delta F^{(e)}=-k_BT\ln Z_p \ .$$

In principle this calculation is not easy because in the variational procedure which consists in minimizing the free energy as a function of R, it is clear that R and δS also depend on the polarization ↑ and ↓ of the electron, so that a self-consistent treatment of $\delta F^{(e)}$, R, and δS is required. At the present time, let us restrict ourselves to the case $\Delta \gg k_BT$. In that case, only the ground state is populated and Δ is too large to allow any fluctuation between the spin ↑ and ↓ states, so that $\mathscr{S}_1=0$, and

$$\delta F^{(e)}=n_d\mathscr{E}_- \ . \tag{2.32}$$

The entropy $\mathscr{S}_2$ can be deduced from the Boltzman formula $\mathscr{S}_2=k_B\ln\Omega$ where Ω is the number of configuations:

$$\Omega=N_d!/[n_d!(N_d-n_d)!] \ .$$

By the use of the Sterling formula, we get

$$\mathscr{S}_2=-k_B\left[n_d\ln\frac{n_d}{N_d}+(N_d-n_d)\ln\left[1-\frac{n_d}{N_d}\right]\right] . \tag{2.33}$$

The quantity $\mathscr{S}_3$ is more difficult to calculate, and some approximations are further required for that purpose which depend on the material which we consider. Therefore, we keep the formal expression $\mathscr{S}_3$ for the purpose of generality and we shall calculate this quantity in the next section. We are now in position to give the expression of the free energy of the bound magnetic polarons per unit cell: $F_p=\mathscr{F}_p/N_u$, where N_u is the number of unit cells,

$$F_p=\frac{N_d}{N_u}\left[y_p\left[\frac{\hbar^2}{2mR^2}-\frac{32e^2}{\pi R^4\kappa_0}\int_0^\infty\frac{dk}{\epsilon(k)[k^2+(4/R^2)]^2}-\frac{\Delta}{2}\right]-k_BT[y_p\mathscr{S}_3-y_p\ln y_p-(1-y_p)\ln(1-y_p)]\right] , \tag{2.34}$$

where $y_p = n_d/N_d$ is the probability that the magnetic polaron is bound. This is the result of Ref. 13, except for a term $(k_B n_d \ln 2)/N_0$ which is missing in Eq. (2.34) because we have assumed $\Delta \gg k_B T$. In Ref. 13 we had made the assumption that the bound electron had an equal probability of occupying the spin-up or -down states. This clearly corresponds to the approximation $k_B T \gg \Delta$ to calculate $\delta F^{(e)}$, and in that case the fluctuations between the two spin orientations give the contribution $k_B \ln 2$ per bound electron to the entropy $\mathscr{S}_1$. This approximation, however, is consistent neither with the results of our calculation nor with the experiments which show that $\Delta \gg k_B T$ even in the paramagnetic phase of EuO. The condition $\Delta \gg k_B T$ is also fulfilled in the case of semimagnetic semiconductors. For example at temperatures of interest for experiments, the bound electron (which in the occurrence is a hole) is found totally spin polarized in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$.[24] It follows from this discussion that the introduction of this entropy term in Ref. 13 was a mistake, which, however, modifies the numerical results only quantitatively.

D. Thermodynamic equilibrium

In europium chalcogenides, we must also consider the electrons in the $(4f)^7$ level located at an energy E_g below the bottom of the conduction band. Their contribution to the free energy can be approximated by[13]

$$F_f = -y_f E_g - k_B T[\,y \ln 4 - y_f \ln y_f - (1-y_f)\ln(1-y_f)\,] , \qquad (2.35)$$

where y_f is the probability that a $(4f)^7$ state is occupied. The first term is the internal energy and the other terms are configurational entropies similar to $\mathscr{S}_1$ and $\mathscr{S}_2$ for the bound polaron. E_g is the energy gap between the $(4f)^7$ level and the conduction band.

To account for transport properties of EuO we have also introduced a number N_A of compensating impurities.[25,26] Such impurities do not provide any significant contribution to the free energy because $N_A/N_u \ll 1$, and only contribute to the equation of neutrality,

$$N_e = \frac{N_d}{N_u}(1-y_p) + (1+y_f) - \frac{N_A}{N_u} . \qquad (2.36)$$

Equations (2.19) and (2.15) determine σ as a function of N_e and T. So the only independent variables of the problem are y_p, y_f, R, T. The thermodynamic equilibrium at a given temperature T is then obtained by the minimization of the total free energy $F_e + F_M + F_p + F_f$ with respect to y_p, y_f, and R with the constraint of Eq. (2.36).

It is now necessary to carry out explicit calculations of two fundamental parameters, $\delta S(\vec{r})$ and $\mathscr{S}_3$. These parameters control all the properties of the bound magnetic polaron because they contain all their specificity with respect to usual bound states. The approximations which can be used to evaluate these two parameters differ essentially according to the strength of the exchange interaction, which is strong in magnetic semiconductors, and small in semimagnetic semiconductors where the mean distance between localized spin is large. We shall then investigate separately the two cases.

III. CASE OF STRONGLY BOUND MAGNETIC POLARON: EuO

A. Results

In EuO the exchange interaction is large and, in practice, fully polarizes the localized spins inside the bound polaron. According to this picture, we can approximate $\delta S^z(r)$ by

$$\delta S^z(\vec{r}) = (S-\sigma)\Theta(R-r) , \qquad (3.1)$$

where Θ is the step function. In such a case, all the N_s localized spins inside the bound magnetic polaron loose their contribution $-\partial F_M/\partial T$ to the magnetic entropy since such spins cannot fluctuate with respect to the other ones. Such a polaron occupies a volume $\frac{4}{3}\pi R^3$ so that

$$N_s = 16\pi R^3/(3a'^3) ,$$

and we have[13]

$$\mathscr{S}_3 = -16\pi \frac{\partial F_M}{\partial T} \frac{1}{3a'^3} . \qquad (3.2)$$

Let us now investigate the numerical results of Sec. II with this particular choice of δS^z and $\mathscr{S}_3$. For the longitudinal dielectric function $\epsilon(\vec{q})$ entering Eqs. (2.26), we have chosen the expression derived by Kübler and Vigren,[8]

$$\epsilon(q) = 1 + \frac{4\pi e^2}{\kappa_0 q^2 V} \left[\chi_0^+(\vec{q}) - \frac{J^2}{N_0} \chi_{zz}^H(\vec{q}) \chi_{0\uparrow}(\vec{q}) \chi_{0\downarrow}(\vec{q}) \right] \left[1 - \frac{J^2}{4N_0} \chi_{zz}^H(\vec{q}) \chi_0^+(\vec{q}) \right]^{-1} . \qquad (3.3)$$

χ_0^+ and $\chi_{0\uparrow,\downarrow}$ have been defined in Eqs. (2.6) and (2.7). Let us recall that N_0 is the number of localized spins and V is the volume of the crystal. χ_{zz}^H is the Kawasaki-Mori susceptibility[27] at zero frequency,

$$\chi^H_{zz}(\vec{q})=\frac{1}{S\sigma}\left[\sum_{\vec{k}}(\psi_{\vec{k}}-\psi_{\vec{k}+\vec{q}})\right]\left[\sum_{\vec{k}}(J_{\vec{k}}-J_{\vec{q}})\psi_{\vec{k}}+(J_{\vec{k}}-J_{\vec{k}+\vec{q}})\psi_{\vec{k}+\vec{q}}\right]^{-1}, \qquad (3.4)$$

where

$$\psi_{\vec{k}}=\left[\exp\left[\frac{g\mu_k H_{\text{ext}}+(\sigma/2)(J_0-J_{\vec{k}})}{k_B T}\right]-1\right]^{-1}. \qquad (3.5)$$

The numerical applications have been performed with the parameters used and justified in Ref. 15, namely $J=0.15$ eV,[28,29] $a'=5.14$ Å,[30] $W=1.1$ eV,[31] $I_1=9\times10^{-5}$ eV, and $I_2=1\times10^{-5}$ eV,[32] where I_1 and I_2 are the exchange constants $I(R_{ij})$ between nearest and next-nearest neighbors, respectively. The background dielectric constant is $\kappa_0=23.9$,[33] and $E_g\sim1.1$ eV.

The electronic phase diagram in the (n_D,T) plane is reported in Fig. 1, where $n_D=n_d/V$ is the concentration of donor sites. For comparison we have also reported in the same figure the previous result of Ref. 8 (dashed line) and the results predicted by the Mott criterium (dotted curve). Within a simple Thomas-Fermi theory the Mott condition which determines the critical density of the carriers n_c^M in the paramagnetic phase is[34]

$$n_c^M(T>T_C^0)\simeq(0.25/a_0)^3\ , \qquad (3.6)$$

where T_C^0 is the Curie temperature of insulating EuO. In our model constructed on the basis of the molecular-field approximation,

$$T_C^0=\frac{S(S+1)}{3k_B}(12I_1+6I_2)\ . \qquad (3.7)$$

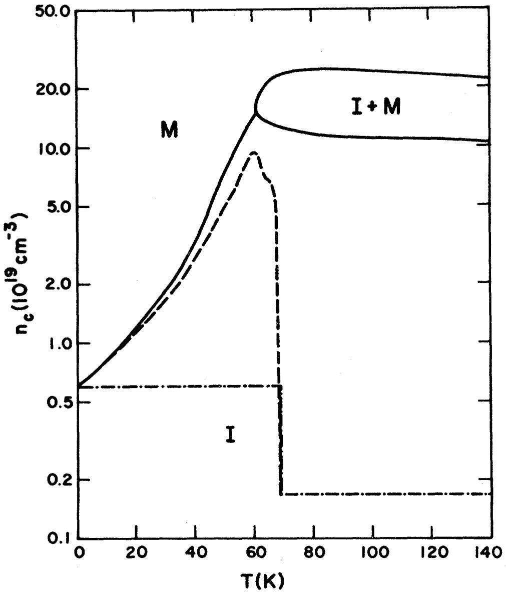

FIG. 1. Electronic phase diagram and critical carrier density n_c as a function of temperature in EuO. Solid curves present the result of the present model. Dashed curve is the result of Kubler and Vigren (Ref. 8). Dotted-dashed lines are normal Mott transitions with exchange-split bands below $T_C=69.4$ K. I is the insulating phase, M is the metallic one, and $I+M$ denotes the mixed phase.

With the values of I_1 and I_2 above mentioned, we get $T_C^0=69.4$ K, in agreement with experiment. a_0 is the Bohr radius of the crystal

$$a_0=\kappa_0\hbar^2/(me^2)\ ,$$

where m is the effective mass at the bottom of the conduction band deduced from Eq. (2.21),

$$m=\frac{2\hbar^2}{Wa'^2}\ . \qquad (3.8)$$

With the values of W and a' mentioned above, we find $m/m_0=0.52$, where m_0 is the mass of the free electron in the vacuum, quite close to the value 0.55 chosen in Ref. 8 in agreement with optical data.[35] Equation (3.6) shows that $n_c^M\propto m^3$ which evidences a very strong dependence of the transport properties on m, contrary to the case of magnetic properties. That is why emphasis has been given to the necessity of choosing the appropriate dispersion relation $E^0(k)$ to reproduce this parameter. At $T<T_C^0$ the electron gas is fully polarized in the spin-up conduction band,[15] which affects the critical Mott concentration for the carriers,[8]

$$n_c^M(T<T_C^0)=4n_c^M(T>T_C^0)\ . \qquad (3.9)$$

The departure of n_c from n_c^M can be regarded as the magnetic polaron effect and is responsible for the particular properties of this material. As an illustration, we have reported in Figs. 2 and 3 the resistivity and magnetization data of some samples together with our theoretical curves. Experimental data have been taken from Refs. 36 and 37. Samples 5—8 are Eu-rich EuO. Since it proves impossible to get large concentrations of oxygen vacancies in bulk EuO, the higher donor concentrations have been provided by substituting Gd for Eu ions and samples 12, 13, and 15 are $Eu_{1-x}Gd_xO$ samples. In particular, it has been shown that bound magnetic polarons can form around oxygen vacancies or around Gd^{3+} ions as well, because the localized spin of Gd^{3+} is $S=\frac{7}{2}$ like that of Eu^{2+}; so that the potential in both cases is essentially restricted to the Coulomb potential $e^2/\kappa_0 r$ of the extra charge.[36,38]

TABLE I. Main transport properties of various samples of n-type EuO. Data from Eu-rich samples are from Refs. 37 (samples 5, 6, and 8) and 40 (samples 4a and 4b). Gd-doped samples 12, 13, and 15 are from Ref. 36.

Sample no.	ρ 4.2 K (Ω cm)	ρ 300 K (Ω cm)	E_A (meV)	n 4.2 K (cm^{-3})	n 300 K (cm^{-3})
5	$>10^{12}$	9×10^{7}	450		
6	$<10^{7}$	10^{7}	270		
12	50	5.1×10^{5}	320		
8	1.1×10^{-3}	1.7	nonactivated	1.1×10^{13}	8.4×10^{18}
4a	6.3×10^{-4}	6×10^{-2}	nonactivated	3.4×10^{19}	5.5×10^{18}
4b	8.3×10^{-4}	5.6×10^{-2}	nonactivated	3.2×10^{19}	6.2×10^{18}
13	8×10^{-4}	4×10^{-3}	nonactivated	8×10^{13}	1.5×10^{20}
15	5×10^{-5}	4×10^{-3}	nonactivated	5×10^{20}	8×10^{20}

Table I provides the main data which characterize these samples. As in Ref. 13, the theoretical resistivity curves have been calculated with the assumption of a carrier mobility $\mu=1$ cm$^2/v_{\rm xs}$ in the paramagnetic configuration and $\mu=10^{-2}$ cm$^2/v_{\rm xs}$ in the ordered phase to reproduce typical experimental values. We have chosen $N_A/N_u=1.66\times10^{-5}$, which amounts to a concentration of acceptor impurities equal to 5×10^{17} cm^{-3}.

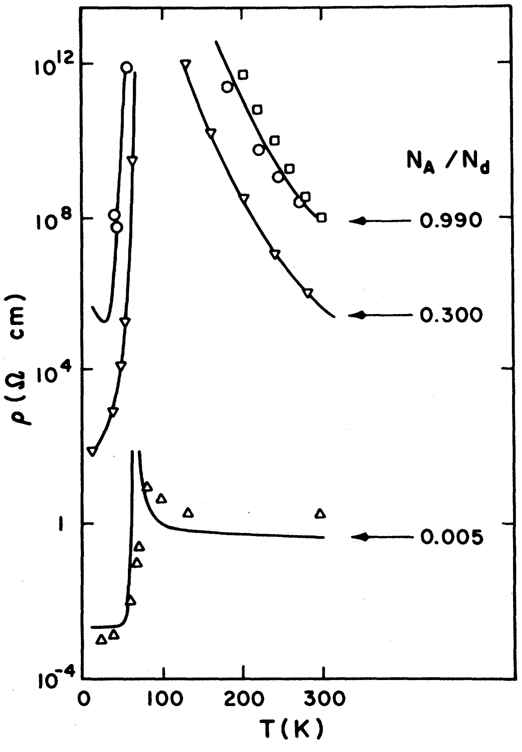

FIG. 2. Resistivity as a function of temperature in EuO. Solid curves are theoretical curves for various rates of compensation N_A/N_d. Acceptor concentration is 5×10^{17} cm^{-3} in all cases. Data points from Ref. 37 are reported for the samples 5 (□), 6 (○), 12 (▽), and 8 (△), listed in Table I.

B. Analysis

1. *In the limit $T=0$*

At $T=0$, both $\delta S(\vec r)$ and $\mathscr{S}_3$ vanish so that the problem is reduced to the simple case of a hydrogenoid donor impurity in nonmagnetic semiconductors. Our model predicts a critical donor concentration $n_c(T=0)$ which is in agreement with Eq. (3.9), namely $n_c \sim 6\times10^{18}$ cm^{-3}. In particular, when $n_D > n_c$, *all* the donors are ionized and the resistivity saturates at low temperatures (see the curves with $N_A/N_d=0.3$ and 0.05), in agreement with experiment. When $n_D < n_c$, the binding energy E_d of the donor level is finite and results from a compromise between kinetic and Coulomb energies. E_d is defined by the energy of the donor level below the bottom of the spin-up conduction subband. In our

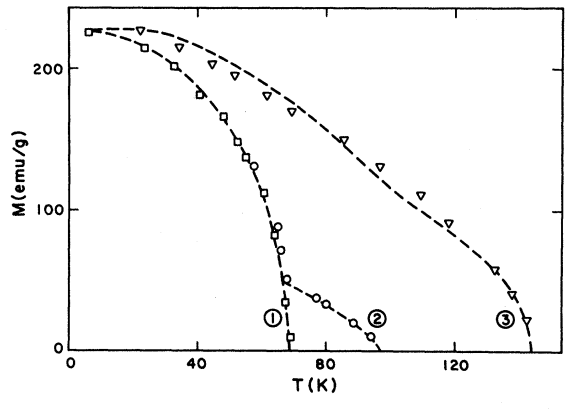

FIG. 3. Magnetization at zero external field as a function of temperature in Gd-doped EuO. Dashed curves are theoretical curves computed in our model for rates of compensation $N_A/N_d \geq 0.1$ (curve 2) and $N_A/N_d=10^{-3}$ (curve 3). Acceptor concentration is 5×10^{12} cm^{-3}. Experimental points for samples 12 (□), 13 (○), and 15 (▽), listed in Table I, are from Ref. 36.

model this quantity is derived from Eqs. (2.26) and (2.27), and taking into account that since $\Delta \gg k_B T$, only the case of a fully polarized bound electron is to be retained;

$$E_d = -\frac{\hbar^2}{2mR^2} + \frac{32e^2}{\pi R^4 \kappa_0} \int_0^\infty \frac{d^3k}{\epsilon(k)(k^2+4/R^2)^2} + \frac{2J}{\pi^3 R^4} \int_0^\infty \frac{\delta S_k^z d^z k}{(k^2+4/R^2)^3} . \tag{3.10}$$

When $n_D < n_c$, E_d is equal to the hydrogenoid binding energy $E_d = 17$ meV, and the radius of the orbit is equal to the Bohr radius $R = a_0$ so that $R \gg a'$. This binding energy gives rise to an activated regime of the resistivity at temperatures such that $k_B T < E_d$, and is responsible for the increase of the theoretical resistivity upon cooling in the case $N_A / N_d = 0.99$ in Fig. 2. Such a feature has been observed experimentally.[39]

2. *In the ferromagnetic phase*

In the range $0 < T < T_C$ our results do not strongly differ from the model of Kübler and Vigren. The main result is that n_c strongly depends on temperature, and then departs from the Mott concentration given by Eq. (3.9). The Mott transition is obtained when N_d is varied, but since n_c^M does not depend on temperature (except around T_C), the Mott model cannot account for the metal-insulator transition as a function of temperature at fixed N_d, which is the particularity of EuO. We can see in Figs. 1 and 2 that our model accounts for such a metal-insulator transition at $T \sim 50$ K for a given $N_D = N_d / V$ in the range $10^{19} < N_D < 10^{20}$ cm^{-3}, in agreement with experiment. I have already outlined the origin of this transition in Ref. 16 where only the magnetic energy was considered. In that case, starting with the assumption that all the donors are ionized, an instability was found at $T \sim 50$ K for such donor concentrations, correlated to a first-order magnetic phase transition which is evidence of instability of the metallic state. In this regard, this previous work is an approach of the metal-insulator transition from the insulating phase.

We can explain this transition as follows: At finite temperature $T \ll T_C$ the entropy $\mathscr{S}_3$ no longer vanishes and the exchange energy associated with δS^z becomes important. At $T \sim 50$ K, the exchange energy due to $\delta \mathscr{S}^z$ becomes large compared to the kinetic plus Coulomb terms in Eq. (3.10). This is the reason why the predictions formulated in Ref. 16 on the consideration of exchange energy alone are confirmed. Then the binding energy of the polaron is essentially equal to the exchange energy, and according to Eq. (3.1) we can write

$$E_d \sim \tfrac{1}{2} JS(1-\sigma) . \tag{3.11}$$

It follows that E_d is much larger than 17 meV in the range 50 $K < T < T_C$. This simply means that the magnetic interactions contribute to localize the electrons around the donor sites, rising up to 10^{20} cm^{-3}, the donor concentration beyond which the metallic phase becomes stable in this range of temperatures. This increase of E_d and the localization of the magnetic polaron is associated with a shrinking of the orbital with a radius in the range $a' < R < a_0$ for $n < 10^{20}$ cm^{-3}.

For samples which exhibit such a metal-insulator transition the magnetization curve does not significantly depart from the Brillouin curve, with a Curie temperature $T_C \sim 69.4$ K as in pure stoichiometric EuO, because the indirect exchange $J_{\text{eff}}(R_{ij})$ vanishes at $T > 50$ K (see curve 1 in Fig. 3). The heavily doped samples ($N_D \sim 5 \times 10^{20}$ cm^{-3}) are metallic and the indirect exchange raises T_C up to $T_C \sim 150$ K. However, the magnetization curve strongly departs from the Brillouin law because J_{eff} depends on σ and then on temperature[15] (curve 3 in Fig. 3). The results agreee with experiment and with our previous calculations.[15] The magnetic behavior of sample 8 is more complex and we shall return to this intermediate case later.

3. *In the paramagnetic phase*

At $T > T_C$ the results of our model are significantly different from the previous models which, contrary to experiment, predicted a second insulator-metal transition for donor concentrations slightly higher than the Mott critical concentration.

To the contrary, in our model, the insulating phase is stable in the wide range of temperatures investigated $T_C < T < 300$ K for donor concentrations $N_D \leq 10^{20}$ cm^{-3}. In the range $10^{20} < N_D < 2 \times 10^{20}$ cm^{-3}, a mixed phase is found (see Fig. 1). Those results come from the fact that at such temperatures $T\mathscr{S}_3$ cannot be neglected. The effect of the entropy $\mathscr{S}_3$ is to localize the electron strongly on the donor site in a molecular orbital the radius of which has the same order of magnitude as the lattice parameter $R \sim a'$ for $n < 10^{20}$ cm^{-3}. In effect, the shrinking of the orbital insures that a minimum of entropy $|\mathscr{S}_3|$ is lost in the formation of the bound magnetic polaron (BMP). Of course this shrinking of the orbital raises the kinetic energy of the bound electron, but the kinetic energy plus the Coulomb energy remain negligible with respect to the exchange energy like in the range $T < T_C$, and Eq. (3.11) becomes (in eV)

$$E_d \sim \tfrac{1}{2} JS \sim 0.3 . \tag{3.12}$$

It follows that in the case $N_D < 10^{20}$ cm^{-3}, the resistivity above T_C is activated and can be written

$$\rho(T) \propto e^{-E_a/(k_B T)} ,$$

where the activation energy E_a varies continuously from $E_d \simeq 0.3$ eV when $N_d \gg N_A$ up to $E_g/2 \propto 0.6$ eV when $N_d \sim N_A$, depending on the degree of compensation of donor and acceptor states. This is in agreement with experiment.[12] The values of E_a are also reported in Table I for the samples used in the present paper.

In the range $10^{20} < N_D < 2\times 10^{20}$ cm^{-3} the solution of our model is a mixed phase. The particular property of this phase is that it has a metallic character in the sense that the resistivity is not activated and is practically temperature independent: $E_A \sim 0$, although all the donors are not ionized. To explain this feature we notice that, in the paramagnetic configuration $|T\mathscr{S}_3| > E_d$ under the effect of thermal fluctuations, a part of the donor assembly is ionized. This is the source of the electron gas which is degenerate in this range of free-carrier concentrations $\sim 10^{19}$ cm^{-3} so that $E_A = 0$. Nevertheless, further electrons which jump in the conduction band get a kinetic energy $\sim E_F$ because of the Pauli principle and Fermi-Dirac statistics, and E_F increases significantly with the free-carrier concentration according to Eq. (2.19). Then, if $|T\mathscr{S}_3| \leq E_d + E_F$, a complete ionization of the bound magnetic polarons is too expensive in kinetic energy. As an example, for a donor concentration $n \sim 2.5\times 10^{20}$ cm^{-3}, we find a free-carrier concentration $n \sim 2.2\times 10^{19}$ cm^{-3}. This prediction of our model is in very good agreement with experiment since Hall-effect measurements have evidenced a free-carrier concentration about 5 times smaller at $T > T_C$ than at $T < T_c$ for such donor concentrations.[40] (See samples 4a, 4b, and 8 in Table I). This can be understood by the fact that at $T \ll 50$ K the samples are in the metallic phase ($N_D > 10^{19}$ cm^{-3}) so that all the donors are ionized and provide their extra electron to the conduction band. But at $T > T_C$ only a fraction of $\sim \frac{1}{5}$ of such magnetic polarons are ionized and contribute to the Hall effect.

As can be seen from Fig. 1 and Table I, sample 8 is quite close to the critical concentration n_0^c above which, according to our model, the insulating phase is not stable at any temperature. As a matter of fact, the magnetic properties of this sample are those predicted for a donor concentration $N_D = 1.2\times 10^{20}$ cm^{-3}, corresponding to $N_D < n_0^c$. Then the material should be insulating in the temperature range $58 < T < 68$ K, giving a Brillouin curve close to that of insulating EuO in agreement with experiment, but then a transition to the mixed phase restores our indirect exchange $J_{\text{eff}}(R_{ij})$, so that the bulk magnetization vanishes only at $T \sim 96$ K. It follows that the tail in the magnetization curve observed between 70 and 96 K may be an intrinsic property. The theoretical curves of the resistivity and magnetization in absence of external field are reported in Figs. 2 and 3 in the case $N_D = 1.2\times 10^{20}$ cm^{-3} together with the experimental data. The large increase of resistivity in the range $60 < T < 70$ K is not observed experimentally. A broad peak of resistivity is indeed observed, but its amplitude is small so that such a peak can be imputed to a critical scattering of the free carriers by spin fluctuations.[41] It follows that the resistivity curve for this sample is fitted by the theoretical curve with $N_d = 1.5\times 10^{20}$ cm^{-3} (above n_0^c), where the mixed phase remains stable in this range of temperatures. We can then infer that the transport and magnetic experiments have probed two different parts of the same ingot with donor concentrations N_D quite close to each other, but on both sides of n_0^c.

C. DISCUSSION

The model of the magnetic polarons has not been the only one considered in the recent past to explain the metal-insulator transition in EuO. In particular, various authors have tried to explain this behavior by considering a hypothetical density of localized states below the bottom of the conduction band.[42] The width Δ of this density tail in the energy scale is then chosen *a priori* equal to 0.3 eV to account for the activiation energy of the resistivity in the paramagnetic configuration. When N_D increases, so does E_F and the material is insulating at $T = 0$ up to the critical donor concentration characterized by $E_F = \Delta$. Then the supplementary donors contribute to the conduction since E_F becomes larger than the mobility gap Δ. At this stage, we can point out some disagreements with experiment, which were not mentioned before: Although a Mott-type transition is observed at low temperature, with a *discontinuous* variation of the free-carrier concentration as a function of N_D for a critical concentration $N_D = N_c^M$, such a model predicts a *continuous* variation of the free-carrier concentration n, with n equal to $N_D - N_c^M$ when $N_D > N_c^M$. In the same way, this model also predicts a *continuous* variation of the activation energy E_A of the resistivity at $T > T_c$, although a *discontinuous* variation is expected since no experimental values of E_A have been reported in the range $0 < E_A < 0.27$ eV for n-type EuO. We can then conclude that such a model does not account for any physical properties of EuO. In fact, such models belong to a series of independent works which attributed the outstanding properties of EuO to disorder effects,[43–45] although we have proved that they are intrinsic properties of this material,[15,16,38] so that we shall not consider them any more. To the contrary, it is clear that our model accounts for all the experimental features above mentioned, and we shall then focus the discussion on the concept of the bound magnetic polaron.

1. In the ferromagnetic configuration

In the previous paragraph, we have pointed out the fact that at $T<T_C$ the entropy $\mathscr{S}_3$ is not yet too important and the magnetic exchange energy associated with the formation of the bound magnetic polaron makes the fundamental difference with the classical hydrogenic bound state. This energy comes from the redistribution δS^z of the localized spins [see Eq. (2.27)]. If follows that the various models of the magnetic polarons in magnetic semiconductors at $T<T_C$ can be essentially characterized by the different procedures used to calculate δS^z.

By analogy with Eq. (2.23) in the Fourier space we can write

$$\delta S^z_{\vec{k}} = L_{21}(k)\varphi(k) \propto \chi^H_{zz}(k)\varphi(k)\ . \tag{3.13}$$

$L_{21}(k)$ is proportional to $\chi^H_{zz}(k)$ because δS^z depends directly on the short-range correlation between the localized spins, i.e., the correlations between spins separated by a distance $r\leq R$, where R is the radius of the orbit, which is also the spatial extension of δS^z. First models calculated δS^z_k from Eq. (3.13).[6,8] However, Leroux Hugon has chosen for χ^H_{zz} the Ornstein-Zernicke function,

$$\chi^H_{zz} = \frac{1}{c_J}\left[k^2+\frac{2J_0}{c_J}\frac{(T_C-T)}{T_C}\right]^{-1}\ , \tag{3.14}$$

where the coefficient c_J is defined by the expression

$$J_k = J_0 - c_J q^2 \tag{3.15}$$

valid at long wavelength: $qa'\gg 1$. This Ornstein-Zernicke expression is known for its inability to describe the short-range correlations since this formula is derived for classical spins in a mean-field approximation. As a consequence this choice of χ^H_{zz} leads to a drastic underestimation of δS^z in Eq. (3.13). This is the basic reason why the results of Ref. 6 do not differ significantly from those of the Mott transition for hydrogenoid impurities given by Eqs. (3.6) and (3.7). In particular, Kübler and Vigren have shown that when a realistic value of m is injected in the equations this model does not account for the metal-insulator transition in EuO at $T\sim 50$ K. To the contrary, the choice of the Kawasaki-Mori susceptibility for χ^H_{zz} provided results in much better agreement with experiment.[8] We impute this success to the fact that such a susceptibility is suitable to describe correlations distant by $r\sim R$.

At high temperatures, however, δS^z is large, so that any calculation of this quantity in a linear-response formalism is questionable. That is why in Ref. 13 and also in this paper we have chosen another approach which consists in choosing δS^z according to Eq. (3.1) rather than to calculate it self-consistently from Eq. (3.13).

More recently Kuivalainen *et al.*[46] have calculated δS^z in a nonuniform mean-field approximation, since they have included $\delta S(\vec{r})$ to $\langle S^z\rangle=\sigma S$ in the expression of the effective magnetic field H in Eq. (2.10) which becomes $\vec{r}$ dependent: $H\rightarrow H(\vec{r})$. Then the free energy F_n is calculated from Eq. (2.12),

$$F_M(\vec{r}) = -xk_BT\ln\left[\sum_{m=-S}^{+S} e^{g\mu_B mH(\vec{r})/k_BT}\right]\ , \tag{3.16}$$

and Eqs. (2.15) and (2.16) are calculated with y replaced by $y(\vec{r})$. Then $\delta S^z(r)$ is deduced from the minimization of the total free energy. (In Ref. 46, F_{tot} was restricted to F_e+F_m.) The results are not markedly different from these of our model at $T<T_C$, but differences are not negligible at higher temperatures as can be seen in Fig. 4 where we have reported the spatial variations of δS^z which we have calculated in both models. This figure illustrates that the mean-field approach of Ref. 46 smears out the variations of $\delta S^z(r)$, which leads to quantitative disagreement with experiment concerning especially the activation energy of the resistivity at high temperature. In particular, the spin polarization does not saturate even at the donor site. This feature is again an illustration that the mean-field approach underestimates δS^z, and consequently, the binding energy of the bound magnetic polaron, although in the present case, the polaron is not unstable as in Ref. 6.

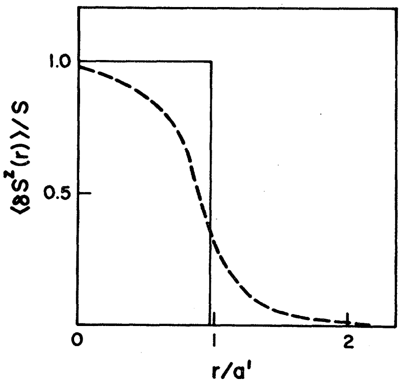

FIG. 4. Localized spin polarization inside a bound magnetic polaron as a function of the distance from the donor site r according to our model (solid curve) and the model of Ref. 46 (dashed curve) for EuO at $T=200$ K with a donor concentration 3×10^{19} cm^{-3}.

2. *Paramagnetic configuration*

Above the Curie temperature, the entropy $\mathscr{S}_3$ was found to be of primary importance in localizing the magnetic polaron. That is why the models prior to Ref. 13 failed to find a stable insulating phase for donor concentrations up to 10^{20} cm^{-3}. To overcome this difficulty, Kübler and Vigren added a perturbative nonuniform magnetic field $h(q)$ to enhance the magnetic field associated with the formation of the bound magnetic polaron. Such a magnetic field can be generated by the localized charge and spin densities due to the electron Ψ itself. In our model, the energy associated with such an effective molecular field should be given by the term $\delta^{(2)}E$ in Eq. (2.30). Yanase and Kasuya[3,47,48] have shown that in some cases this field can cause a self-trapped magnetic polaron to form near T_C. However, we have shown that there is no experimental evidence of such a polaron in EuO,[49] and we can assume with a good approximation $\delta^{(2)}E \simeq 0$. The other effect invoked to introduce $h(q)$ is related to the inner electron bound on the oxygen vacancy.[8] However, the arbitrary introduction of $h(q)$ is not sufficient to increase significantly the critical donor concentration above which the insulator configuration becomes unstable above 100 K, while it increases this concentration up to a much too high value below T_C. Moreover, it has been proved that the experimental properties do not depend on the nature of the donors (oxygen vacancy or Gd^{3+} ion), but only on their concentration.[36–38] This implies that the effective field $h(q)$ mentioned in Ref. 8 taking its origin from a special feature specific to one kind of donors should be negligible. We shall then consider that the only effect of this feature, namely the existence of the inner electron in the oxygen vacancy, it to screen the double charge of the vacancy to reduce the perturbing potential to the repulsive Coulomb potential of a single charge $e^2/\kappa_0 r$ chosen in our model.

In Ref. 13, we could account for the existence of bound magnetic polarons at temperatures well above T_C because $\mathscr{S}_3$ was already calculated from Eq. (3.2). The more recent work of Kuivalainen *et al.*[46] also accounts for such an effect, and this is illustrated in Fig. 4. We can explain this result as follows: The difference between Eqs. (3.6) and (2.13) is just the quantity δF_M which we have defined in Eq. (2.19), and we can write

$$\delta F_M = \delta^{(2)}E - T\mathscr{S}_3 = F_M(\vec{r}) - F_M \ . \qquad (3.17)$$

This important equation shows that in Ref. 46, $\mathscr{S}_3$ was implicitly taken into account, although it was not explicated in their paper.

It turns out from the above discussion that the model in Ref. 46 differs from our model in Ref. 13 or in the present paper essentially in the nature of the approximations used to calculate δS and $\mathscr{S}_3$. The calculation of these quantities in the mean-field approximation (MFA) in Ref. 46, however, leads to some discrepancies with experiment. For example, when calculating the magnetization curve from Eq. (3.16), a large magnetization at zero field is found well above T_C,[46] in complete disagreement with experiment (see Fig. 3). The reason for this spurious result is that σ as deduced from Eq. (3.16) includes the contribution of the bound magnetic polarons. However, this contribution is calculated in the MFA which is not valid in the present case because the mean distance between the polarons is large compared with the range of the magnetic interactions. The MFA amounts to the approximation that the range of the interactions is infinite, and implies that the directions of the mean spin polarization of each bound magnetic polaron are aligned parallel with each other, providing a substantial resulting component to the magnetization at $T > T_C$ because the spins inside each polaron are strongly polarized. In our model, this procedure would consist in calculating the contribution of the polarons to σ from Eq. (2.27) where z is the axis of quantification for the spins (either imposed by an external field or by the effective field ΔB^z of Ref. 46). In fact, it is clear that in Eq. (2.27), z should be considered as a *local* axis, which determines the direction of the mean polarization inside our particular polaron, but this direction is random from one magnetic polaron to another one, because they are separated by a too large distance and can be considered as independent. That is why we have chosen the opposite approximation which consists in neglecting the contribution of the bound magnetic polarons to the magnetization, and simply calculated σ from Eq. (2.15). At $T > T_C$, this is justified for the above-mentioned reasons. At low temperature it is justified because the number of spins inside the polarons is small compared with the full number of magnetic spins in a magnetic semiconductor; of course, this is not true in a semimagnetic semiconductor and we shall return to this point later.

We have also pointed out that the calculation of δS and $\mathscr{S}_3$ in the MFA leads to some disagreement with experiments concerning the transport properties, such as a too small value of E_a, for example. In fact, almost all the exchange energy $\frac{1}{2}JS(1-\sigma)$ is gained in the formation of the bound magnetic polaron. For low donor concentrations our model is then quite close to that developed in Refs. 4 and 50, where the donor level is supposed to be decoupled from the conduction band at an energy independent of temperature from the $(4f)^7$ level at $T < 50$ K. Then at $T \lesssim 50$ K the bottom of the conduction band crosses the donor level due to the exchange interaction in Eq. (2.3) and the donor states become delocalized. We agree with this picture of the metal-insulator transition in EuO for donor concentrations in the range $10^{19} < N_d < 10^{20}$ cm^{-3}, when Eqs. (3.11) and (3.12) are valid. However, such a description is incomplete since it does not provide any explanation for the experimental results at other donor concentrations. Moreover, even in the range $10^{19}-10^{20}$ cm^{-3}, such a model is not valid at $T \sim 50$ K. For example, it predicts a continuous decrease of the binding energy which vanishes at $T \sim 50$ K. To the contrary, according to our model, E_d varies discontinuously at this temperature, which means that the metal-insulator transition is first order. The variations of E_d in our model are reported in Fig. 5 for two different donor concentrations.

3. Dynamic stability of the uniform metallic state

In the previous model, we have assumed *a priori* that the uniform metallic state was stable when the donor sites are ionized. The purpose of this paragraph is to discuss the validity of such an assumption. It has been shown that when Eq. (3.14) is used, all terms involving J^2 in Eq. (2.26) can be reduced to give a factor[6,8]

$$j = \frac{(JS)^2 \kappa_0}{\pi e^2 c_J} \frac{V}{N_0} . \tag{3.18}$$

The metallic uniform state will be unstable if the equation

$$L_{ij}(k)^{-1} = 0 \tag{3.19}$$

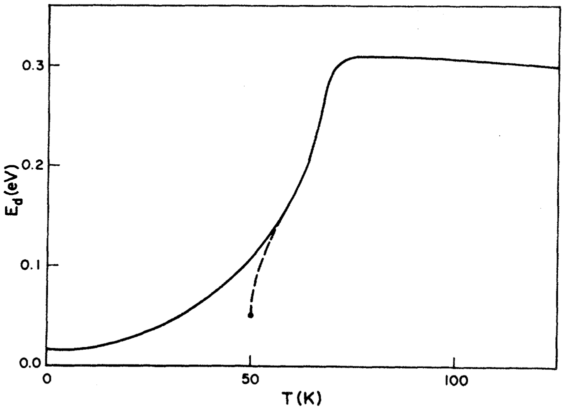

FIG. 5. Theoretical variations of the binding energy E_d of the bound magnetic polaron in EuO as a function of temperature, for donor concentrations 10^{18} cm^{-3} (solid curve) and 7×10^{19} cm^{-3} (dashed curve). In the later case, a metal-insulator transition takes place at 50 K with a discontinuous jump of E_d.

has a solution for real positive values of k. The linear-response coefficients L_{ij} have been defined in Eqs. (2.23) and (3.13). Equation (3.19) is equivalent to

$$k^4 + k^2(k_s^2 + \lambda^2 - jk_s^2) + k_s^2\lambda^2 = 0 . \tag{3.20}$$

This last equation is the direct consequence of Eq. (10) in Ref. 6, or of the expression of ξ in Eq. (32) of Ref. 8. λ^{-1} is the correlation length of the spins and k_s is the Thomas-Fermi inverse screening length,

$$\lambda^2 = \frac{J_0}{c_J} \frac{T - T_C}{T_C}, \quad k_s^2 = \frac{6\pi^2 n}{\kappa_0 E_F} . \tag{3.21}$$

n is the free-carrier concentration. Positive values of k^2 are solutions of Eq. (3.20) if and only if

$$j \geq \left[1 + \frac{\lambda}{k_s} \right]^2 , \tag{3.22}$$

in which case the solutions are

$$k_{+,-}^2 = k_0^2 \pm (k_0^4 - k_3^2\lambda^2)^{1/2} , \tag{3.23}$$

where

$$k_0^2 = \frac{jk_s^2 - \lambda^2 - k_s^2}{2} . \tag{3.24}$$

When condition (3.22) is fulfilled, the uniform metallic state is unstable with respect to static spin- and charge-density waves of vector k_+ and k_-. In the same way, we have calculated numerically the dynamic stability of the uniform metallic state from the response coefficients $L_{ij}(k,\omega)$ determined in the random-phase approximation in Ref. 8. The dispersion equation for the fluctuations is given by

$$L_{ij}(k,\omega)^{-1} = 0 . \tag{3.25}$$

This equation which gives the dispersion relation of the spin- and charge-density waves is found to have solutions $\omega(k)$ in the whole range $k_- < k < k_+$ if and only if Eq. (3.22) is fulfilled. This condition, however, is more stringent than the approximate formula in Eq. (11) of Ref. 6. Let us now evaluate numerically the coefficient j. Kübler and Vigren[8] have taken $c_J = 2I_1 a'^2$, which is the value expected if $J_{\vec{k}}$ is restricted to $I_{\vec{k}}$ in Eq. (2.11). In that case $j \sim 90$, and according to Eq. (3.22) the uniform metallic state is not stable. Then an arbitrary value $j \sim 0.9$ has been chosen[8] although the authors recognized there was no convincing argument to reject the value of j given by Eq. (3.18) in favor of one that is smaller. We believe that this difficulty is due to the fact that in Ref. 8, the contribution of J_{eff} in Eq. (3.11) has been forgotten in the calculation of c_J defined in Eq. (3.15). The variations of the Fourier transform of $J_{\rm eff}(R_{ij})$ have been studied in detail in Ref. 15; they modify j by a typical factor 10^2 and leads to $j \sim 1$. The reason of this drastic effect of $J_{\rm eff}(R_{ij})$ is that this indirect exchange interaction is long range, contrary to the superexchange mechanism $I(R_{ij})$, so that the Fourier transform is sharply peaked at $q=0$, and increases c_J by a factor $(l/a')^2$ where the length l characterizes the spatial extension of $J_{\rm eff}(R_{ij})$. It follows that condition (3.22) is not fulfilled so that the uniform metallic state in heavily doped EuO is always stable and our model is valid.

In EuS, however, some authors have reported that the uniform metallic state should be unstable with respect to charge- and spin-density waves,[51,52] which means that in EuS the condition (3.22) can be satisfied for some definite free-carrier concentration n entering k_s in Eq. (3.21). The calculations of the dynamic stability in Refs. 51 and 52 are rather different from the present ones since they are based on an hydrodynamic approach of the localized spin system, but the results are essentially the same. In particular, it is also found that the spin- and charge-density waves which are stable have wave vectors k in a definite range $k_- < k < k_+$ around a mean value k_0 with values of k_+, k_-, and k_0, which differ according to the model, but which have always the same order of magnitude ($k_0 \sim 10^{-6}$ cm). Initially these theoretical works[51,52] on EuS aimed to explain particular experimental properties,[53] and it is not established that there is any metal-insulator transition in EuS. The lack of such a transition would be in agreement with a nonuniform ground state. However, to our knowledge, there does not exist any systematic study of the physical properties of EuS as a function of the sulfur-vacancy concentration. It follows that on an experimental point of view, the debate is still open but that the extension of our present model to this compound is not justified.

IV. EXTENSION OF THE MODEL

A. Polarons in semimagnetic semiconductors

Magnetic polarons may also take place in semimagnetic semiconductors. The concept of the magnetic polaron as developed in Sec. II can be readily applied to $\mathrm{Cd}_{1-x}\mathrm{Mn}_{1-x}\mathrm{Se}$ because this material is n type and the free carriers (electrons in the conduction band) are in s states and carry a spin $\frac{1}{2}$. In $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$, trivial changes in the above model must be made to take into account that the material is p type, so that the free carriers which localize to form bound magnetic polarons are now holes in p states which carry on angular momentum $\frac{3}{2}$. In both cases, the Mn^{2+} ions carry a spin $S=\frac{5}{2}$. Under some aspects, the description of a magnetic polaron in such materials is much simpler. First the impurity concentration is always very low, so that the insulating phase is always stable. It follows that in our model $F_{\rm tot}$ can be reduced to F_M+F_p since the free-carrier concentration is too small to give any significant contributions to $F_{\rm tot}$ and there are no $4f$ electrons in these compounds. Once again, the problem is then to calculate δS^z and $\mathscr{S}_3$. Contrary to the case of EuO, the distance between magnetic ions is now large compared with the lattice constant a'. As a consequence, the magnetic polarons are much more spread out, and the molecular-field approach is a better approximation. That is why the existing models calculate δS^z and $\mathscr{S}_s$ in the MFA.[51,52] In Ref. 51, Dietl and Spalek also considered the case of high temperature where the bound carrier is not fully spin polarized, and calculated $\delta F^{(e)}$ in Eq. (2.30) assuming implicitly that R and δS^z did not depend on the spin polarization of the electron. In this case Eqs. (2.26) and (2.32) give

$$\delta F^{(e)}=n_d\mathscr{E}_- - k_BT\ln\left[2\cosh\left[\frac{\Delta}{2k_BT}\right]\right] . \qquad (4.1)$$

However, we could not find any justification for this assumption and such an expression of $F^{(e)}$ [which leads to Eq. (2) in Ref. 51] can only be considered as an approximation. Fortunately, as we already pointed out, the trapped change is fully spin polarized at temperature of interest.[24] In such a case, the spin density of this charge is simply $|\Psi(\vec{r})|^2$ and Eq. (2.2) reads

$$H_1=-\int |\Psi(\vec{r})|^2\frac{J}{2}\langle S(r)\rangle d^3r . \qquad (4.2)$$

Here we have taken the continuum approach for the localized spins, which is justified because $R \gg a'$. Equation (3.2) corresponds to the molecular field

$$H(\vec{r})=\frac{J|\Psi(\vec{r})|^2}{2g\mu_B} , \qquad (4.3)$$

and we can then derive $F_M(\vec{r})$ defined in Eq. (3.16). Two limits can be considered.

(a) $H(\vec{r}) \gg H_{\rm ext}$, where $H_{\rm ext}$ is the external field (if any). Equation (2.15) reads

$$\delta S^z(r)=SB_S\left[\frac{SJ|\Psi(r)|^2}{2k_BT}\right] , \qquad (4.4)$$

and the magnetic energy of the polaron is then[24]

$$E_M=\frac{S}{2}J\int d^3r\,|\Psi(r)|^2B_S\left[\frac{SJ|\Psi(r)|^2}{2k_BT}\right] . \qquad (4.5)$$

In particular the spin-flop energy for the bound electron defined in Eq. (3.27) is $\Delta=2E_M$, and if the Brillouin function $B_S(y)$ is developed up to the first order in y, we get

$$\Delta=\frac{(2S+1)^2-1}{24}J^2\int d^3r\frac{|\Psi(r)|^4}{k_BT}\;. \tag{4.6}$$

With $S=\frac{5}{2}$, the numerical factor is $\frac{35}{24}\sim\frac{3}{2}$ and we can write

$$\Delta\sim\frac{2W'^2}{k_BT}\,, \tag{4.7}$$

where

$$W'^2\simeq 3(J/2)^2\sum_i|\Psi(R_i)|^4$$

in the notation of Ref. 52, where the continuum approximation is not used and the factor $\frac{1}{2}$ in Eq. (4.3) is absorbed by a different definition of J. A more refined treatment leads to[52]

$$\Delta=\frac{2W'^2}{k_BT}+\frac{4k_BTW'^2}{(kT)^2+W'^2}\;. \tag{4.8}$$

This expression reduces to Eq. (4.7) when $kT\ll W'$, but gives $\Delta\sim 6W'^2/k_BT$ when $k_BT\gg W'$, i.e., an enhancement by a factor of 3 due to the fact that at high temperature the crude MFA underestimates $\mathcal{S}_3$ and Δ as was done for EuO, as discussed in Sec. III.

(b) $H_{\rm ext}\gg H_1$; in this case, we can write

$$S(\vec r)=SB_S\left[\frac{g\mu_BSH_{\rm ext}}{k_BT}+\frac{SJ|\Psi(\vec r)|^2}{2k_BT}\right]. \tag{4.9}$$

The Taylor expansion of this formula up to the first order in H_1 gives

$$\delta S^z(\vec r)=\chi(T,H_{\rm ext})\frac{J|\Psi(\vec r)|^2}{2(g\mu_B)^2}\,, \tag{4.10}$$

where $\chi(T,H_{\rm ext})$ is the magnetic susceptibility of the localized spins without the contribution of the bound magnetic polarons. Now the magnetic energy associated with the formation of the bound magnetic polaron is

$$E_M(T,H)=(J/2)^2\frac{\chi(T,H)}{(g\mu_B)^2}\int|\Psi(r)|^4d^3r\,, \tag{4.11}$$

or, after integration,

$$E_M=\frac{1}{4}\frac{J^2\chi}{(g\mu_B)^2\pi R^3}\,, \tag{4.12}$$

which is 8 times larger than the value of ϵ_p found in Ref. 51. Moreover, the authors in Ref. 51 have extended Eq. (4.10) to the case $H_{\rm ext}\ll H_1$ which is not justified, and leads to spurious results we shall now analyze.

The case $H_{\rm ext}\gg H_1$ is quite analogous to the situation $T\sim 0$ in EuO: The bulk spin polarization σ is larger so that $\mathcal{S}_3$ is negligible. When extending the above equations to the case $H_{\rm ext}\sim 0$, the authors in Ref. 51 have then underestimated $\mathcal{S}_3$. This can be evidenced by noticing that δF_M defined in Eq. (3.18), is simply proportional to E_M when calculated from Eqs. (4.9) and (4.10). This is the result of Dietl *et al.* if we notice that, according to Eq. (4.10), the parameter η in Ref. 51 is

$$\eta=\chi\frac{J}{2(g\mu_B)^2}\frac{1}{\pi R^3}\;.$$

It follows that $\mathcal{S}_3$ is not properly taken into account in Eq. (2.30). The results are then easy to understand. The temperature associated with the magnetic interactions is the Curie temperature T_C in EuO (ϵ_p/k_B in semimagnetic semiconductors). In EuO we have explained that the models which neglect $\mathcal{S}_3$ predict that the bound magnetic polarons do not exist at $T\geq T_C$. For the same reasons, the same models predict that the bound magnetic polarons do not exist ($\Delta=0$) at temperatures $k_BT>\epsilon_p$ in semimagnetic semiconductors.[51]

The authors in Ref. 51 have then calculated separately $\mathcal{S}_3$. In effect, their quantity $p(\Delta)$ can be considered as a number of configurations with a given Δ, to which is associated an entropy $\mathcal{S}_3=k\ln p(\Delta)$. With this regard, the procedure used in Ref. 51 which consists in choosing the value of Δ which corresponds to the maximum of $p(\Delta)$ is then equivalent to calculate $\mathcal{S}_3$ from the second law of thermodynamics for thermally isolated systems.

It follows that this model also differs from previous ones only by the choice of approximations to calculate $\mathcal{S}_3$. However, there is a misunderstanding in Ref. 51 since the authors imputed some irrelevant results to the MFA. In fact, the spin splitting of the bound magnetic polaron persists at high temperature even in the MFA, and the irrelevant results $\Delta=0$ is due to erroneous evaluations of δS^z and $\mathcal{S}_3$ which have nothing to do with the MFA.

Also these authors[51] claim that the calculation of the bound magnetic polaron in Ref. 46 led to a critical temperature T_p through the divergence of the static susceptibility. in fact this susceptibility can be decomposed into $\chi+\chi_p$, where χ_p is the magnetic polaron part and χ is the unperturbed susceptibility, as in Eq. (4.10). Of course, we agree with Ref. 51 that the magnetic polaron susceptibility χ_p cannot be determined in the MFA, as explained in Sec. III, but the spurious peak of χ_p at $T_p=\epsilon_p/k_B$ when χ_p

is calculated in the MFA for a semimagnetic semiconductor[51] should not be confused with the peak of χ at T_C in a ferromagnet. It is clear that in Ref. 46 the divergence, in agreement with experiments, occurs at the Curie temperature T_C, and is a divergence of χ. This property is thus independent of the magnetic polaron itself (except that T_C depends on the free-carrier concentration) in EuO or EuS. As mentioned in Sec. III, the spurious result in Ref. 46 is not the peak of susceptibility as presumed in Ref. 51, but the fact that $\sigma \neq 0$ far above T_C. Note that in semimagnetic semiconductors even χ cannot be derived in the MFA because irreversible effects take place: A peak of the reversible part of χ can still be observed, but it is connected with the susceptibility of mictomagnets and spin-glasses.[53,54] However, neither in Ref. 51 nor in Ref. 52 was χ studied, and only the temperature dependence of χ_p was investigated in these papers. In semimagnetic semiconductors, the resistivity has not been measured in detail, mainly because these materials are insulating, and we cannot, as in EuO, compare the results of the model with any activation energy E_A. We can, however, compare the calculation of the spin-flip transition energy $\hbar\omega_0$ with optical data. We can deduce from Refs. 51 and 52 that the model of the magnetic polaron very well accounts for the temperature and field dependence of $\hbar\omega_0$ both in $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ and $\mathrm{Cd}_{1-x}\mathrm{Mn}_x\mathrm{Se}$, a result which we had clearly inferred for EuO.[49,55]

B. Entropy effects in other materials

Recently, Dietl and Spalek[14] reproduced our conclusion[13,38] that the electron in the magnetic polaron further lowers its energy as it aligns its spin with the local magnetization created by thermodynamic flucuations. This, however, is nothing but the conclusion of our previous works on the magnetic polarons.[13,38] But even then, we certainly do not claim such an originality: The entropy (or thermodynamic fluctuations) play a similar role in other various metal-insulator transitions. For example, in a quite different context, Kaplan *et al.*[56] studied the Hubbard Hamiltonian for a half-filled band and showed that also in this case entropy terms draw a metal-semiconductor transition as T increases. On another subject, Falicov *et al.*[57] pointed out the importance of magnetic entropy effects in metal-insulator transitions occurring in $(\mathrm{V}_{1-x}\mathrm{Cr}_x)_2\mathrm{O}_3$. These authors deduced their results from a calculation including magnetic interaction to the model of Falicov *et al.*[58] known to account for various aspects of mixed-valence phenomena. According to our present model, we can still go further in the comparison with mixed-valence systems. In particular, we have shown that for a definite range of donor centers our model predicts a mixed phase, where the proportion of ionized donors is not close to an integer (0 or 1) but has an intermediate value (typically $\frac{1}{5}$). This leads to the conclusions that also in mixed-valence systems the magnetic entropy may have important effects; on this topic, we can already notice that some disagreements between experiment and predictions of the model developed in Ref. 58 concerning some properties of SmS have been imputed to the fact that the magnetic entropy associated with the localized spins were not taken into account, although its contribution is fundamental to stabilize the insulating state at high temperature.[59] Under this aspect our model of the magnetic polaron has a certain generality and gives a contribution to a better understanding of the metal-insulator transitions in magnetic semiconductors.

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