

Bound Magnetic Polarons in Antiferromagnetic Semiconductors

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We discuss properties of bound magnetic polarons in an antiferromagnetic semiconductor placed in an external magnetic field. When the strength of the exchange coupling between the electron spin and local moments is increased, there can be an abrupt transition between a large and a small bound magnetic polaron. Associated with the bound state is a large ferromagnetic moment; our theory provides a quantitative account of magnetization data on EuTe.

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Magnetic semiconductors are insulators at zero temperature; one of the atomic constituents carries a localized spin S . An excess electron (in the conduction band) couples to the local moments via a strong exchange interaction, typically ferromagnetic in sign. If the electron is localized in a bound state near a donor, it induces ferromagnetic order in the near vicinity of the donor via this exchange, increasing its binding energy in the process. This is a bound magnetic polaron (BMP). The BMP has been the subject of many theoretical studies in ferromagnetic semiconductors such as EuO and EuS.¹ However, when the temperature $T=0$, the spins are already fully aligned in these materials, and the BMP reduces simply to a classical hydrogenic state unaffected by the conduction-electron-local-moment exchange.

Quite to the contrary, in antiferromagnetic semiconductors, even at $T=0$, coupling of the donor electron to the local moments strongly modifies the

BMP, as we shall see. This Letter discusses such states, and points out that they are the origin of the "ferromagnetic clusters" observed in EuTe.² Indeed, we obtain quite a nice account of the data with the calculations reported below. Our interpretation thus differs from that given earlier, which views² the ferromagnetic clusters as associated with "ferrons," which are electrons far from donor sites, self-trapped in a potential well produced by ferromagnetic alignment of local moments induced by the conduction-electron-local-moment exchange. In work described elsewhere,³ we have reexamined the theory of ferrons, and concluded that no such entities exist, for parameters characteristic of EuTe.

We describe the antiferromagnetic semiconductor as a continuum, characterized by the spin density $\vec{S}(\vec{r}) = \sum_i \vec{S}_i \delta(\vec{r} - \vec{R}_i)$. With V_c the volume of the unit cell, nearest-neighbor antiferromagnetic exchange, and a Zeeman field parallel to the \hat{z} axis, the Hamiltonian of the host is

$$\mathcal{H}_0 = \frac{1}{2} J V_c \sum_{\vec{r}} \int d^3 r \vec{S}(\vec{r}) \cdot \vec{S}(\vec{r} + \vec{\delta}) - g \mu_B H_0 \int d^3 r S_z(\vec{r}). \quad (1)$$

We ignore anisotropy here, so that the spins are in the spin-flop state in the presence of the magnetic field H_0 .

In these materials, the conduction-electron bandwidth W is large compared to the conduction-electron-local-moment exchange A . This has the following consequence. While each individual localized spin has a nonzero transverse moment, this oscillates in sign as one moves from site to site, and as the conduction electron hops rapidly through the lattice, it averages over the transverse moments associated with the spin-flop state. Then it senses only their \hat{z} components, which for all local moments are positive and nonzero in this configuration. The electron spin is thus directed along \hat{z} , and

we have for its spin density $\vec{s}(\vec{r}) = \hat{z} |\psi(\vec{r})|^2 / 2$, with $\psi(\vec{r})$ the spatial portion of its wave function. The expectation value of the conduction-electron-local-moment exchange is then

$$V_{st} = -\frac{1}{2} A V_c \int d^3 r S_z(\vec{r}) |\psi(\vec{r})|^2. \quad (2)$$

We calculate the total energy of the system by adding to Eq. (1) (we treat the host spin density classically) the electron energy

$$E_e = T_e + V_{st} - V_d - \mu_B H_0, \quad (3)$$

where $V_d = -(e^2/\epsilon) \int d^3 r |\psi(\vec{r})|^2 / r$ is the potential energy provided by the donor site, and T_e

$= + (\hbar^2/2m) \int d^3r |\nabla\psi(\vec{r})|^2$ is the kinetic energy. Here m is the effective mass at the bottom of the conduction band, and ϵ is the dielectric constant of the matrix.

We are assuming the adiabatic approximation (A is much larger than the local-moment-local-moment exchange J), and that a host spin at \vec{r} makes the angle $\theta(\vec{r})$ with the \hat{z} direction. Minimization of the total energy with respect to $\theta(\vec{r})$ gives, with z the number of nearest neighbors,

$$\cos\theta(\vec{r}) = \frac{g\mu_B H_0}{4zJS} + \frac{AV_c}{8zJS} |\psi(\vec{r})|^2, \quad (4)$$

an expression that is valid so long as the right-hand side is less than unity. To obtain Eq. (4), we assume that $\theta(\vec{r})$ varies sufficiently slowly in space so that the sum $\sum_{\vec{\delta}} \cos\theta(\vec{r} + \vec{\delta})$ over the set of neighbors nearest to the local moment at \vec{r} may be replaced by $z \cos\theta(\vec{r})$. We are to replace the right-hand side of this expression by unity [then $\theta(\vec{r}) = 0$] when the right-hand side becomes greater than 1. Then the strength of the local-moment-conduction-electron exchange is sufficiently large to fully polarize the core of the BMP; we have a ferromagnetic core surrounded by a "halo" within which the ferromagnetic moment of the spin-flop state is enhanced.

When A is sufficiently small that the core never saturates, one obtains a simple expression for the energy ΔE of the BMP, relative to the bottom of the conduction band:

$$\Delta E = T_e - \frac{1}{2} V_I - V_d \quad (5)$$

where

$$V_I = \frac{A^2 V_c}{16zJ} \int d^3r |\psi(\vec{r})|^4. \quad (6)$$

Our task is now to find the function $\psi(\vec{r})$ everywhere, with the BMP core unsaturated. We have now mapped our problem onto one of the cases considered by Emin and Holstein,⁴ in their simple but elegant analysis of a class of polaron problems treated within the adiabatic approximation. Their analysis, applied here, provides insight into the problem. Replacing $\psi(\vec{r})$ by $R^{-3/2}\psi(\vec{r}/R)$, and letting T_e , V_I , and V_d be the relevant quantities calculated for $R = 1$, we have

$$\Delta E(R) = \frac{T_e}{R^2} - \frac{1}{2} \frac{V_I}{R^3} - \frac{V_d}{R}, \quad (7)$$

and assume for the moment that $\psi(\vec{r})$ produces a minimum in $\Delta E(R)$ at $R = 1$. This leads to the relation

$$V_d = T_e + (T_e^2 - \frac{3}{2} V_I V_d)^{1/2}. \quad (8)$$

With $A = 0$ ($V_I = 0$), we have $V_d = 2T_e$, the well-known virial theorem result, and a hydrogen $1s$ state $\psi(r) = \exp(-r/r_0)/(\pi r_0^3)^{1/2}$ as the ground state with $r_0 = \hbar^2 \epsilon / m e^2 = a_B$, where a_B is the Bohr radius. As A increases, T_e rises above $V_d/2$, a consequence of the shrinking of the orbital radius, eventually to the point where the square root in Eq. (8) vanishes. Here we have $V_d = T_e$, $V_I = 2T_e/3$, and then $r_0 = a_B/2$, if we use the hydrogenic wave function with R_0 as the variational parameter. The square root vanishes when $A = A_c^{(1)}$, where

$$A_c^{(1)} = 8\hbar (\pi z J a_B / 3 m V_c)^{1/2}. \quad (9)$$

The decrease in r_0 with increasing A can be limited by saturation of spin polarization within the core of the BMP. If we require the core to just saturate when $r_0 = a_B/2$, we find that this occurs when $A = A_c^{(s)}$, and

$$A_c^{(s)} = (1 - H_0/H_c) zJS \pi a_B^3 / V_c, \quad (10)$$

with $H_c = 4zJS/g\mu_B$. This is the field which pulls the spin-flop phase of the bulk material into a fully aligned ferromagnetic state [set $A = 0$ and $\theta(\vec{r}) = 0$ in Eq. (4)]. For fixed J , $A_c^{(1)} \sim a_B^{1/2}$ while $A_c^{(s)} \sim a_B^3$. Hence for large a_B , and $H_0 \ll H_c$, we have $A_c^{(s)} > A_c^{(1)}$, and so we hit the point where the square root vanishes *before* the core saturates. In the opposite limit $A_c^{(s)} < A_c^{(1)}$, the core reaches saturation first. For the two cases, one traces out the following behavior:

(a) $A_c^{(s)} > A_c^{(1)}$.—As A increases from 0 to $A_c^{(1)}$, r_0 decreases continuously from a_B to $a_B/2$. For $A > A_c^{(1)}$, $\Delta E(R)$ no longer has a minimum at finite R ; $\Delta E(R) \rightarrow -\infty$ as $R \rightarrow 0$, which means in this regime we have only a small BMP with a radius of the order of a lattice constant. As A passes through $A_c^{(1)}$, the radius r_0 of the BMP drops abruptly from $a_B/2$ to a lattice constant. Our theory cannot treat this second regime.

(b) $A_c^{(s)} < A_c^{(1)}$.—As A increases from 0, r_0 decreases from a_B to a value $r_1 > a_B/2$, where the core begins to saturate. The decrease of r_0 with further increase in A is small because the increase in kinetic energy associated with decreasing r_0 is less efficiently offset by an increase in magnetic exchange binding energy. Through use of our hydrogenic function, we have constructed a phase diagram of the BMP, as a function of $A_c^{(s)}$ and A . This is Fig. 1.

When the core is saturated, the energy function ΔE no longer has the simple form given above; Emin-Holstein scaling no longer leads to useful

results. We have now, after some algebra,

$$\Delta E = \frac{1}{2} N_c g \mu_B H_c S \left[1 - \frac{H_0}{H_c} \right]^2 - \frac{1}{2} A S \left[1 - \frac{H_0}{H_c} \right] \int_{r < r_c} d^3 r |\psi(\vec{r})|^2 + T_e - \frac{1}{8} \frac{A^2 V_c S}{H_c} \int_{r > r_c} d^3 r |\psi(\vec{r})|^4 + V_d, \quad (11)$$

where N_c is the number of unit cells in the core. The first term in Eq. (11) is the difference in energy between local moments in the core fully aligned in the magnetic field H_0 , and that of the spin-flop state spread over the same volume, while the second and third terms describe the interaction energy between the electron and the local moments, taking due account of the fact that $\theta(\vec{r}) = 0$ when $r < r_c$. For the hydrogenic form of the variational wave function, the core radius r_c is given by, with the volume of the unit cell in EuTe written as $V_c = a^3/4$,

$$\exp\left[-\frac{2r_c}{r_0}\right] = \frac{8\pi r_0^3}{a^3} \frac{g\mu_B H_c}{A} \left[1 - \frac{H_0}{H_c} \right]. \quad (12)$$

We shall want to calculate the magnetic moment associated with this state:

$$M = g\mu_B S \left[N_c + V^{-1} \int_{r > r_c} d^3 r \cos\theta(\vec{r}) \right]. \quad (13)$$

The change in magnetic moment ΔM_{BMP} associated with the BMP may be written

$$\Delta M_{\text{BMP}} = g\mu_B S \left[\frac{AV_c}{2H_c} + N_c - \frac{AV_c}{2H_c} \int_0^{r_c} d^3 r |\psi(\vec{r})|^2 \right], \quad (14)$$

independent of field H_0 , as long as $H_0 \ll H_c$. If there are N_D donors present, each with a bound electron, and the centers are independent, $N_D \Delta M_{\text{BMP}}$ is then the change in moment of the whole sample.

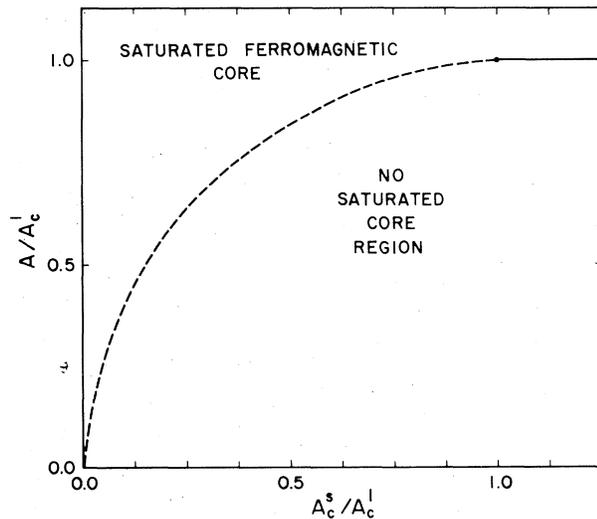


FIG. 1. The phase diagram of the BMP, as a function of A , deduced through use of a hydrogenic orbital in the variational calculation. As the solid line is crossed in the direction of the increasing A , there is a sudden collapse of the BMP from a "large" to a "small" state. For $A_c^{(s)}/A_c^{(1)} < 1$, the dashed line delineates the boundary between the region where the core is saturated, and that where it is unsaturated.

We now apply the above picture to EuTe. Here we have^{2,5} $S = \frac{7}{2}$, $g = 2$, $\epsilon = 8$, $A = 0.15$ eV, $m/m_0 = 0.4$ (m_0 is the free electron mass), and $H_c = 75$ kG. For the fcc lattice, $V_c = a^3/4$ with $a = 6.6$ Å in this case. Therefore $a_B = 10.6$ Å, $A_c^{(1)} \cong 0.09$ eV, and $A_c^{(s)} \cong 0.011$ eV for $H_0 = 0$. We are thus in the case $A_c^{(1)} > A_c^{(s)}$, well into the regime where the core is saturated. We find that the radius r_0 of the hydrogenic $1s$ orbital that minimizes the energy [we use Eq. (11)] is $r_0 = 6.72$ Å; Eq. (12) gives $r_c = 0.994r_0 = 6.7$ Å. Then $\Delta M_{\text{BMP}} = 545\mu_B$, a large value. Although the shrinking of the orbital, $a_B - r_0$, is quite significant, our calculation shows that the main contribution to ΔM_{BMP} comes from the "halo" and not the ferromagnetic core. The halo gives $412\mu_B$ out of the $545\mu_B$, contrary to the common current picture which emphasizes the role of the ferromagnetic core. Vitins and Wachter² have measured the magnetization curve of a doped EuTe sample (their sample 399) which contains a donor concentration sufficiently small that overlap between donors may be ignored. They indeed find a magnetization that can be described as $M = \chi_0 H_0 + N_D \Delta M_{\text{BMP}}$, with χ_0 the susceptibility of EuTe in the flopped state. At low temperatures the free carrier concentration n is small, and N_D can be taken equal to the donor concentration. At room temperature, $n = N_D \times \exp(-E_d/k_B T)$ and from the value of n at room temperature and E_d given by these authors, we find $N_D = 9 \times 10^{18} \text{ cm}^{-3}$. Then our model gives for

$N_D \Delta M_{\text{BMP}}/N$, the average excess magnetization per unit cell generated by the BMP, the value $0.36\mu_B$, in good accord with the data.

As remarked earlier, Vitins and Wachter^{2,5} assumed that ferrons were responsible for the excess magnetization. But at low temperature, very few free carriers are present, and they had to assign an enormous moment ($14000\mu_B$) to each ferron as a consequence. Nearly all the free carriers were in fact frozen out and trapped at the donor sites at low temperature. As we have just seen, the much more modest moment associated with the BMP states provides an explanation for the data. Elsewhere³ we show that for parameters relevant to EuTe, in fact there are no ferrons in EuTe. The same conclusion follows from earlier work of Umehara and Kasuya,⁶ if the parameters deduced by Vitins and

Wachter are employed.

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