Role of conduction-electron—local-moment exchange in antiferromagnetic semiconductors: Ferrons and bound magnetic polarons

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We present a theoretical description of the influence of conduction-electron—local-moment exchange on the properties of free carriers in antiferromagnetic semiconductors, with explicit application to EuTe. We conclude that the ferron, an electron self-trapped in a potential well formed by exchange-induced ferromagnetic polarization of the matrix, does not exist at low temperatures in real three-dimensional antiferromagnets, though it is stable in quasi-one-dimensional systems. An electron bound to a donor site induces a ferromagnetic moment near the donor, and we find that such bound magnetic polaron states account for the ferromagnetic clusters attributed to ferrons in previous studies.

I. INTRODUCTION

The study of the exchange interaction between conduction electrons and localized spins has been a fundamental topic in condensed-matter physics for years. Most studies consider electrons in metals where the strength A of the exchange interaction is very small compared to the Fermi energy E_F. The effects of the exchange coupling are then modest in magnitude, though subtle as illustrated by the Kondo effect.

In magnetic semiconductors, the exchange coupling is very strong, and at the same time characteristic kinetic energies of the free carriers are small, simply because the carrier concentration is small. One may then realize the limit $E_F < A$. The influence of the exchange interaction can be very large and influence numerous properties of the crystal in a dramatic fashion. An example is provided by the temperature variation of the absorption edge in ferromagnetic semiconductors, such as EuO and EuS. The onset of magnetic order shifts the edge to the red,[1] an effect that may be attributed to the influence of the exchange interaction on the self-energy of the free carriers. If the exchange coupling has the form $A\mathbf{S}\cdot\mathbf{s}$ with $\mathbf{S}$ and $\mathbf{s}$ the local moment and conduction-electron spin, respectively, the lowest-order contribution to the self-energy is $\mp\frac{1}{2}A\langle S_z\rangle$ for up and down spin electrons, respectively. The exchange-induced shift of the band edge amounts to a substantial fraction of an electron volt.

This paper addresses influences of the local-moment—conduction-electron exchange in antiferromagnetic semiconductors, with emphasis on application to one much studied material, EuTe. Here, with AS a measure of the conduction-electron—local-moment exchange again, we have $A \gg J$, where J is the strength of the local-moment—local-moment exchange responsible for the antiferromagnetic order. Then, if a conduction electron with spin up is placed in the crystal, and if its wave function is furthermore localized in space, it can induced ferromagnetic order in its near vicinity. This induced order generates a potential well, and in fact the electron may be self-trapped in this fashion to form a magnetic analog of a self-trapped polaron. At low temperatures, where the local-moment spin arrangement in the undoped crystal closely approximates that in the ground state, this possibility for self-trapping exists only in antiferromagnets (or in other arrangements where the full ferromagnetic moment fails to be realized in the ground state). We then have a new type of quasiparticle, intrinsic in character, first introduced by de Gennes.[2] This entity has been the topic of a number of theoretical studies,[3–7] and has been given the name "ferron" by Nagaev.[7]

There is clear experimental evidence for the existence of ferromagnetic clusters in the antiferromagnetic materials EuSe and EuTe.[8] These clusters have been attributed to ferrons, a view supported by theoretical studies[4,5,7] which predict that the ferron state is stable at $T=0$, in EuTe.

In the first part of this paper, we investigate this issue once again. Previous studies confine attention to the case where the external magnetic field is zero, while we include an external Zeeman field H_0. We may then calculate the magnetization of the system explicitly as a function of external field. The model we use is the same as that employed in earlier studies, but our approach is somewhat different. We introduce certain simplifications which we believe have only modest influence on the quantitative predictions of the theory; we are then able to appreciate its overall structure more clearly, and we may draw certain general conclusions as a consequence. In the end, with use of parameters currently believed appropriate for EuTe, we conclude that the ferron state is not stable at $T=0$, in low magnetic field. It is also clear that in one-dimensional antiferromagnets, the ferron state is indeed realized for arbitrarily weak conduction-electron—local-moment exchange.

In these materials, as in any semiconductors, electrons may be trapped at donor sites, bound by the Coulomb potential. Here, however, such bound states lead to an induced ferromagnetic moment in the near vicinity of the donor site. One refers to this entity as the bound magnetic polaron. Earlier work has explored these states in the ferromagnetic semiconductors EuO and EuS,[8] and here we apply our approach to the case where the ground state

is antiferromagnetic. Our calculations show that the ferromagnetic moments induced near donor sites account nicely for the magnetization data in EuTe. The earlier analysis of the data[9] required that one assign an enormous moment ($14\,000\mu_B$) to each ferron. Because nearly all the free carriers are frozen out on donors at low temperatures, a much more modest (but still very substantial) induced moment about each donor suffices.

The organization of this paper is as follows. Section II discusses the physical picture we have in mind, the model, the general structure of the theory, and certain conclusions that may be reached, independent of the choice of variational wave function. Section III presents our variational study of the intrinsic ferron state and the properties of the bound state with application to EuTe. Section IV consists of brief concluding remarks.

II. BASIC MODEL

A. General formulation

There are three energy scales in the problem of interest. The first is set by the strength of the exchange interactions between the local moments. We assume nearest-neighbor, antiferromagnetic exchange of strength J between local moments of spin S. A measure of the strength of the exchange interactions is then provided by the exchange field $H_E=zJS$ exerted on a given spin by its z nearest neighbors. The conduction-electron–local-moment exchange is written $-A\mathbf{S}\cdot\mathbf{s}$, with $\mathbf{s}$ the electron spin so $H_x=AS/2$ is a measure of this energy scale. Finally there is W, the width of the conduction band. The discussion presented below assumes that the three energies are ordered in the following sequence: $H_E \ll H_x \ll W$. This assumption is reasonable for EuTe.

Since $H_x \gg H_E$, the conduction electron may adjust rapidly to the arrangement of the local moments, and motions in the latter system are very slow. We may then invoke the adiabatic approximation, and write the wave function of one electron moving among the spins in the form

$$\Psi(\mathbf{r};\mathbf{S}_1,\ldots,\mathbf{S}_N)=\Psi(r;\{\mathbf{S}_i\}) =\psi_e(r;\{\mathbf{S}_i\})\Phi(\{\mathbf{S}_i\}) , \tag{2.1}$$

where the symbol $\{\mathbf{S}_i\}$ denotes the set of quantum members required to label the states accessible to the system of local moments.

Consider for the moment an electron placed in a state of spin up, confined to a finite volume V. With the electron spin along $\hat{\mathbf{z}}$, each local moment within V is subjected to an effective magnetic field of strength proportional to H_x parallel to $\hat{\mathbf{z}}$. We ignore anisotropy effects on the local moments. In europium chalcogenides, this is justified because the $4f$ shell of the Eu^{2+} ions is half filled so that, in agreement with Hund's rule, the magnetic ions carry a spin $S=\frac{7}{2}$ and are in s states of spherical symmetry ($L=0$). Since $H_x \gg H_E$, the local moments within V will want to assume a spin-flop configuration; since the easy axes of magnetization of the antiferromagnet are the transverse axes, the local moments will adjust themselves so that z is a transverse axis, in order to minimize the indirect exchange energy. The local moments then each have a longitudinal component, in the plane normal to $\hat{\mathbf{z}}$. The sign of this longitudinal component alternates as one moves from local moment to local moment, in the manner characteristic of the spin-flop state. Since $W \gg H_x$, the electron hops very rapidly from site to site and averages over the transverse moment. The average transverse moment it samples is then zero, while all local moments have a positive projection on the z axis (assuming the local-moment–conduction-electron exchange is ferromagnetic in character).

The electronic part $\psi_e(\mathbf{r},\{\mathbf{S}_i\})$ of the system wave function in Eq. (2.1) is then well approximated by a spin-up state and we need not consider an admixture of spin down character in our variational ansatz. In their study of the ferron in zero magnetic field, Umehara and Kasuya[6] allow for such an admixture. If ϕ measures the tilt of the electron spin away from $\hat{z}$, these authors find that when $H_x \ll W$, $\phi \cong (AS\cos\theta/W)$ where θ is the canting angle of the local moments. In the limit of interest here $\phi \cong 0$.

One may appreciate this point in another manner. Let $E(\mathbf{k})$ describe the conduction band, with $A=0$, the consider motion of an electron through a helicoidal state of the local moments, characterized by the wave vector $\mathbf{q}$. The S_+s_- terms mix the spin-up state $\mathbf{k}$ with the spin-down state $\mathbf{k}+\mathbf{q}$, and the renormalized energy bands (in a reduced zone) have the form[10]

$$E_\pm(\mathbf{k})=\tfrac{1}{2}[E(\mathbf{k})+E(\mathbf{k}+\mathbf{q})] \pm\tfrac{1}{2}\{[E(\mathbf{k})-E(\mathbf{k}+\mathbf{q})]^2+(AS)^2\}^{1/2} .$$

As $\mathbf{q}\to 0$ and we have a ferromagnetic array of local moments, one finds $E_\pm(\mathbf{k})=E(\mathbf{k})\pm\frac{1}{2}AS$ exhibiting the large self-energy correction responsible for the shift of the optical absorption edge described earlier. For an antiferromagnet, for wave vectors $\mathbf{k}$ of electrons near the bottom of the conduction band, $E(\mathbf{k})\sim 0$ and $E(\mathbf{k}+\mathbf{q})\sim W$, so we have $E_-(\mathbf{k})\cong E(\mathbf{k})-(AS)^2/2W$. The renormalization of the band edge, which has its origin in the longitudinal spin polarization of the ground conduction states, is now very small when $H_x \ll W$, and the electron is spin polarized along the transverse z axis.

There is one last point. This is that in the Eu chalcogenides, $S=\frac{7}{2}$, so we are also in the limit $S \gg 1$. Because of this, we treat the spins in a classical manner.

B. Variational calculation

The model Hamiltonian is written, in appropriate units ($\hbar=1$),

$$H=-\frac{1}{2m^*}\nabla^2+V(r)+\tfrac{1}{2}\sum_{ij}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j -AV_c\sum_i \mathbf{S}_i\cdot\mathbf{s}\delta(\mathbf{r}-\mathbf{R}_i) -\gamma_s H_0 s_z-\gamma_S H_0\sum_i S_i^z , \tag{2.2}$$

where m^* is the effective mass at the bottom of the con-

duction band, J_{ij} is the (positive) quantity J when i and j refer to nearest-neighbor sites in the lattice, V_c is the volume of the unit cell (associated with the paramagnetic state), and γ_s and γ_S are the Landé g factors of the conduction-electron and local moments, respectively, multiplied by the Bohr magneton μ_B. So long as the function ψ_e in Eq. (2.1) describes an electron in a spin-up state, the term $\gamma_s H_0 s_z$ simply adds a constant to the energy, and this will be dropped in what follows; in addition, we set γ_S equal to unity. Finally, when we examine the possibility that ferrons may exist, we set $V(r)=0$, while a description of the bound magnetic polaron follows by choosing $V(r)=-e^2/\epsilon_0 r$, where ϵ_0 is the background dielectric constant of the crystal. With $\psi_e(\mathbf{x})$ always normalized so

$$\int d^\eta x\, \psi_e^*(\mathbf{x})\psi_e(\mathbf{x})=1 \tag{2.3}$$

(we suppress explicit reference to the dependence of ψ_e on $\{\mathbf{S}_i\}$ henceforth), where η is the dimensionality of the system considered, we have

$$\langle\Psi\,|\,H\,|\,\Psi\rangle=\langle T\rangle+\langle V\rangle+\tfrac{1}{2}\sum_{ij}J_{ij}\langle\Phi\,|\,\mathbf{S}_i\cdot\mathbf{S}_j\,|\,\Phi\rangle - \sum_i\langle\Phi\,|\,S_i^z\,|\,\Phi\rangle[H_0+h(i)]\,, \tag{2.4}$$

where $h(i)$ is an effective magnetic field, parallel to $\hat{\mathbf{z}}$, defined by

$$h(i)=\tfrac{1}{2}AV_c\,|\,\psi_e(\mathbf{R}_i)\,|^2\,. \tag{2.5}$$

Also,

$$\langle T\rangle=-\int d^\eta x\,\psi_e^*\frac{\nabla^2}{2m^*}\psi_e \tag{2.6}$$

with a similar expression for $\langle V\rangle$.

For a particular choice of $\psi_e(\mathbf{r})$, Eq. (2.4) describes an antiferromagnet subjected to a spatially uniform, external Zeeman field H_0, supplemented by the spatially varying piece $h(i)$. Both fields are parallel to $\hat{\mathbf{z}}$. In the absence of anisotropy, the antiferromagnet is in a spin-flop state, with a canting angle that varies with position, in regions of space where $h(i)$ is nonzero. We let the spins lie in the yz plane, with θ_i the angle between $\langle\Phi\,|\,\mathbf{S}_i\,|\,\Phi\rangle$ and the y axis. In our classical treatment of the spin system, at the absolute zero of temperature we have

$$\langle\Phi\,|\,\mathbf{S}_i\cdot\mathbf{S}_j\,|\,\Psi\rangle=\langle\Phi\,|\,\mathbf{S}_i\,|\,\Phi\rangle\cdot\langle\Phi\,|\,\mathbf{S}_j\,|\,\Phi\rangle$$

and we suppose $|\psi_e(\mathbf{r})|^2$ varies sufficiently slowly in space that for nearest-neighbor sites, we may ignore the difference between θ_i and θ_j for nearest-neighbor spins. Then

$$\langle\Psi\,|\,H\,|\,\Psi\rangle=\langle H\rangle=\langle T\rangle+\langle V\rangle-zJS^2\sum_i\cos(2\theta_i) -S\sum_i[H_0+h(i)]\sin(\theta_i)\,. \tag{2.7}$$

If we fix $\psi_e(\mathbf{r})$, then require $\partial\langle H\rangle/\partial\theta_i=0$, we are led to a condition which fixes θ_i:

$$\sin\theta_i=\frac{H_0+h(i)}{2zJS}\,. \tag{2.8}$$

This relation holds if the right-hand side of Eq. (2.8) is less than unity. When $H_0+h(i)>2zJS$, the local effective field is sufficiently strong to fully align the local moments along $\hat{\mathbf{z}}$. If we then choose $H_0>H_c=2zJS$, the spins are fully aligned along $\hat{\mathbf{z}}$ everywhere in the sample. The ferron state is then not possible, since a potential well cannot be created by inducing a ferromagnetic moment, and the donor binding energy is uninfluenced by the conduction-electron—local-moment exchange for the same reason.

We then have the following picture of the spin configuration which surrounds a localized electron state. Far from the center of the state, where $|\psi_e(\mathbf{x})|^2$ is negligible in amplitude, we have the normal spin-flop state in the external field H_0, with canting angle given by the standard expression $\sin\theta=H_0/2zJS$ when $H_0<H_c$. As we move in toward the core of the localized state, $h(i)$ becomes nonzero, the canting angle increases, and we have a region of enhanced ferromagnetic moment. If (for an s state)

$$H_0+\tfrac{1}{2}AV_c\,|\,\psi_e(0)\,|^2<H_c\,, \tag{2.9}$$

then the spin configuration is everywhere of spin-flop character, once again with enhanced amplitude near the core of the state. We call this a type-I localized state (ferron or bound magnetic polaron).

For an s state, there may be a critical radius r_c for which

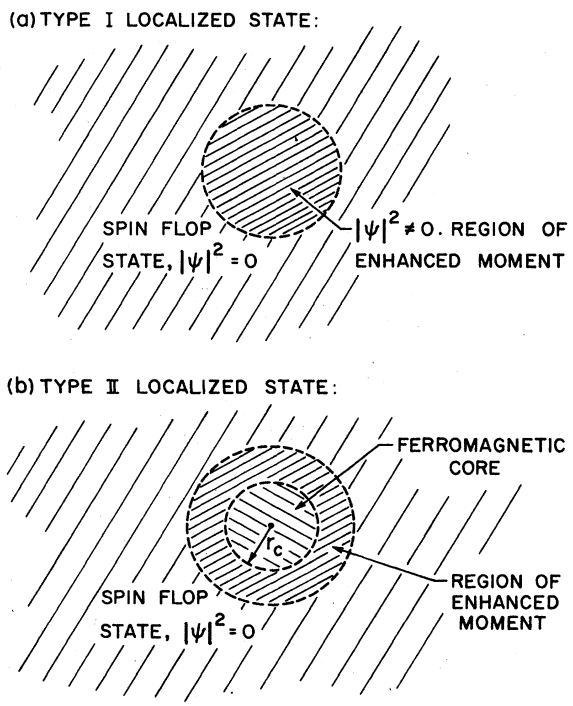

FIG. 1. A schematic illustration of the types of localized states. (a) For the type-I state, one has a region of enhanced ferromagnetic moment in the region where $|\psi|^2\neq 0$, and the spin configuration has spin-flop character everywhere. (b) For the type-II state, one has a ferromagnetic core surrounded by a halo of enhanced moment.

$$H_0+\tfrac{1}{2}AV_c\,|\,\psi_e(r_c)\,|^2\equiv H_c\ , \tag{2.10}$$

and then it follows that for $r_c<r<\infty$ we have a spin-flop configuration, but when $0<r<r_c$, the core has a fully saturated ferromagnetic moment. The state may then be described as a ferromagnetic "bubble," surrounded by a halo within which the ferromagnetic moment is enhanced, associated with the spin-flop configuration. We call this a type-II localized state. These two different situations are illustrated in Fig. 1.

We may now write expressions for the energy of the localized state. It is useful to consider the type-I and type-II states separately, and here we confine our attention to only states of s symmetry.

1. Type-I state (unsaturated core)

In the expression for the total energy, we may use Eq. (2.8) to eliminate the canting angle everywhere. Then the total energy of the system is

$$\langle H\rangle_{\rm I}=E_0+\Delta E_{\rm I}\ , \tag{2.11}$$

where E_0 is the energy of the infinite crystal, with all spins in the spatially uniform spin-flop state, and ΔE the incremental energy associated with the introduction of the excess electron in the matrix, in the localized state. We have, with $H_c=2zJS$, the critical field required to fully align the moments in the infinitely extended crystal,

$$\Delta E_{\rm I}=\langle T\rangle+\langle V\rangle-\frac{S}{2H_c}\sum_i\{[H_0+h(i)]^2-H_0^2\}\ . \tag{2.12}$$

In the spirit of our continuum model,

$$\sum_i\rightarrow\frac{1}{V_c}\int d^\eta x\ ,$$

so we may also write

$$\Delta E_{\rm I}=\langle T\rangle+\langle V\rangle-\frac{SH_0A}{2H_c}\int d^\eta x\,|\,\psi_e\,|^2-\Xi\ , \tag{2.13}$$

where, to simplify the notation, we have introduced Ξ defined by

$$\Xi=\frac{SA^2V_c}{8H_c}\int d^\eta x\,|\,\psi_e\,|^4\ .$$

The integral in the third term of Eq. (2.13) equals unity by virtue of normalization of the electron wave function, so in fact we have simply

$$\Delta E_{\rm I}=\langle T\rangle+\langle V\rangle-\Xi-\frac{1}{2}\frac{SH_0A}{H_c}\ , \tag{2.14}$$

a functional whose properties have been discussed very elegantly elsewhere.[11] We turn to its properties shortly.

2. Type-II state (saturated core for $r<r_c$)

Here we may use Eq. (2.8) only for $r>r_c$, and then for $0\le r\le r_c$ we must take $\theta_i=\pi/2$. The resulting expressions for the energy is written conveniently in terms of the number of spins N_c inside the ferromagnetic core. This is given by

$$N_c=\frac{1}{V_c}\int_{x<r_c}d^\eta x\ . \tag{2.15}$$

After a bit of algebra, we find

$$\Delta E_{\rm II}=\langle T\rangle+\langle V\rangle+\tfrac{1}{2}N_cH_cS\left[1-\frac{H_0}{H_c}\right]^2-\frac{A}{2S}\int_{x>r_c}d^\eta x\,|\,\psi_e\,|^2-\frac{SH_0A}{2H_c}\int_{x>r_c}d^\eta x\,|\,\psi_e\,|^2-\frac{SA^2V_c}{8H_c}\int_{x>r_c}d^\eta x\,|\,\psi_e\,|^4\ , \tag{2.16}$$

which may be rewritten to read

$$\Delta E_{\rm II}=\Delta E_{\rm I}+\tfrac{1}{2}N_cH_cS\left[1-\frac{H_0}{N_c}\right]^2-\frac{A}{2S}\left[1-\frac{H_0}{H_c}\right]\int_{x<r_c}d^\eta x\,|\,\psi_e\,|^2+\frac{SA^2V_c}{8H_c}\int_{x<r_c}d^\eta x\,|\,\psi_e\,|^4\ . \tag{2.17}$$

We conclude this section with some general remarks on the properties of ferrons and bound magnetic polarons, then we present results of a variational study and application to EuTe.

C. General remarks on the properties of ferrons and bound magnetic polarons

When the excess electron is at the bottom of the conduction band, we have the limit of the uniform state, in which case $\psi_e=V^{-1/2}$ with V the volume of the crystal. Substituting this expression in the integrals entering $\Delta E_{\rm I,II}$, we find that in the limit $V\rightarrow\infty$, these integrals vanish so $\Delta E_{\rm I,II}\rightarrow-SH_0A/(2H_c)$. This energy [added to the term $-\gamma_sH_0s^z=-\gamma_sH_0/2$ already dropped in Eq. (2.2)] represents the Zeeman shift of the conduction band in the spin-flop state in the presence of the molecular magnetic field generated by the external field. The energy of formation of the nonuniform state (either ferron or bound magnetic polaron) is thus

$$\mathscr{E}_{\rm I,II}=\Delta E_{\rm I,II}+\frac{SH_0A}{2H_c}\ ,$$

i.e., we must recognize that the bottom of the conduction band shifts, and the energy of interest is measured relative to the shifted band edge.

1. The ferron

Here we have $\langle V\rangle\equiv0$, and the question is then whether the conduction electron can be self-trapped in the potential well it creates through the ferromagnetic moment induced by the local-moment–conduction-electron exchange. One must treat the discussion of the type-I state

separately from that which applies to the type-II state.

Emin and Holstein[11] have presented a very simple but elegant analysis of the functional in Eq. (2.14), though they were interested in a rather different physical situation. We repeat their argument here since it is quite brief. Suppose we evaluate $\Delta E_{\rm I}$ (with $\langle V\rangle=0$ for the moment) for some particular function $\psi_e^{(0)}(\mathbf{x})$. We then repeat the calculation for

$$\tilde{\psi}_e(\mathbf{x})=R^{-\eta/2}\psi_e^{(0)}(\mathbf{x}/R)\ ,$$

where $\tilde{\psi}_e(\mathbf{x})$ is normalized if $\psi_e^{(0)}$ is. Let $\langle T\rangle_0$ be the kinetic energy and $\Xi^{(0)}$ be the value of the integral Ξ, calculated with $\psi_e^{(0)}$. Then as one scales the variational function in the manner described, one finds

$$\mathscr{E}_{\rm I}(R)=\frac{\langle T\rangle_0}{R^2}-\frac{\Xi^{(0)}}{R^\eta}\ . \tag{2.18}$$

a. Three-dimensional case. For $\eta=3$, $\mathscr{E}_{\rm I}(R)$ fails to have a minimum for any finite value of R. Since $\psi_e^{(0)}(\mathbf{x})$ can be any function, it follows that we cannot find a function which yields a minimum in the energy functional. We conclude that in three dimensions, type-I ferrons do not exist. According to Eq. (2.18), as $R\to 0$, $\mathscr{E}(R)\to\infty$, suggesting the possibility of a "small ferron." We must remember, however, that there is always a finite value of R below which the magnetization is saturated in a core region, so Emin-Holstein scaling breaks down and detailed study is required to address the questions of whether or not such states exist. We turn to such a study later.

b. One-dimensional case. Note that for a conduction electron in a one-dimensional antiferromagnet, we do obtain a minimum in $\mathscr{E}_{\rm I}(R)$ for a finite value of $R=R_0=2\langle T\rangle_0/\Xi^{(0)}$, and we have

$$\begin{aligned} R_0&=2\langle T\rangle_0/\Xi^{(0)}\ ,\\ \mathscr{E}_{\rm I}(R_0)&=-\frac{1}{4}\frac{(\Xi^{(0)})^2}{\langle T\rangle_0}\ . \end{aligned} \tag{2.19a}$$

The ferron binding energy $-\mathscr{E}_{\rm I}(R_0)$ is thus positive, with the consequence that in one-dimensional antiferromagnets, we find that type-I ferrons are stable, contrary to the three-dimensional case. Any convenient choice of $\psi_e^{(0)}(x)$ may then be used in Eq. (2.19) to provide a variational estimate of the ferron binding energy. We can choose ψ with a Gaussian profile which describes the spread of the wave packet in one dimension:

$$\psi(x)=\left[\frac{2}{\pi}\right]^{1/4}\frac{1}{(x_0)^{1/2}}e^{-(x/x_0)^2}$$

with x_0 the variational parameter. In this case, Eq. (2.19a) gives

$$\begin{aligned} x_0&=\frac{32J\hbar^2}{\pi^{1/2}maA^2}\ ,\\ \mathscr{E}(x_0)&=-\frac{3\pi}{1024}\frac{ma^2A^4}{\hbar^2J^2}\ . \end{aligned} \tag{2.19b}$$

This discussion assumes that $\theta(x)<\pi/2$. The core begins to saturate if $A=A_c$ such that, according to Eq. (2.9),

$$H_0+\frac{1}{2}\frac{A_c}{a}|\psi_e(0)|^2=H_c\ ,$$

where a is the lattice parameter. With our choice of $\psi_{e'}$, $|\psi_e(0)|^2=(2/\pi)^{1/2}x_0^{-1}$. Then taking Eq. (2.19b) into account, we find

$$A_c=\left[\frac{256}{\sqrt{2}}\frac{\hbar^2J^2S}{ma^2}\left[1-\frac{H_0}{H_c}\right]\right]^{1/3}\ .$$

Note that $\hbar^2/(ma^2)$ is the order of the conduction bandwidth W. For $A=A_c$, Eq. (2.19b) gives the radius x_0^c:

$$x_0^c=\frac{1}{8}\left[\frac{2}{\pi}\right]^{1/2}\left[\frac{\sqrt{2}}{256}\right]^{1/3}a\left[\frac{W}{J}\right]^{1/3}\left[S\left[1-\frac{H_0}{H_c}\right]\right]^{1/3}\ .$$

The numerical factor is small, namely, 0.017. Therefore, for any reasonable value of W/J, one finds that $x_0^c\ll a$, so that when $A\geq A_{c'}$, one has the picture of an electron self-localized on a single site where the local moment is fully spin polarized along the z axis.

In Sec. III, we report a variational study of the possibility that type-II ferrons exist in the three-dimensional antiferromagnetic EuTe.

2. Bound polaron

Now we have $\langle V\rangle\neq 0$, and, in fact, $V=-e^2/\epsilon_0 r$. For the type-I state, this case was also considered by Emin and Holstein. In three dimensions, the scaling argument now gives for a type-I bound polaron

$$\mathscr{E}_{\rm I}(R)=\frac{\langle T\rangle_0}{R^2}-\frac{\Xi^{(0)}}{R^3}-\frac{|\langle V\rangle_0|}{R}\ . \tag{2.20}$$

This function now admits a minimum at finite R, and we assume $\psi_e^{(0)}(\mathbf{x})$ is chosen so this minimum is at $R=1$. We then find an algebraic relation between $\langle T\rangle_0$, $\Xi^{(0)}$, and $|\langle V\rangle_0|$:

$$|\langle V\rangle_0|=\langle T\rangle_0+(\langle T\rangle_0^2-3\Xi^{(0)}|\langle V\rangle_0|)^{1/2}\ . \tag{2.21}$$

When $\Xi^{(0)}=0$ ($A=0$), we have the result $|\langle V\rangle_0|=2\langle T\rangle_0$, well known from the virial theorem. The ground state is the hydrogenic $1s$ orbital $\psi_e(r)=\exp(-r/r_0)(\pi r_0^3)^{-1/2}$, with $r_0=\hbar^2\epsilon_0/m^*e^2\equiv a_B$, the effective Bohr radius.

Suppose we increase A. Then Eq. (2.21) requires $\langle T\rangle_0$ to rise above the virial theorem result $|\langle V\rangle_0|/2$. This means that the radius of the bound state contracts. As A continues to increase, the ratio $\langle T\rangle_0/|\langle V\rangle_0|$ does also until we hit the point where $|\langle V\rangle_0|=\langle T\rangle_0$. The square root in Eq. (2.21) vanishes at that point, so we also have $\Xi^{(0)}=\langle T\rangle_0/3$. If we continue to use the hydrogenic $1s$ orbital as the basis of the variational calculation, the square root vanishes when $r_0=a_B/2$, and when A reaches the critical value $A_c^{(1)}$ given by

$$A_c^{(1)}=\hbar\left[\frac{16\pi H_c a_B}{3m^*V_c}\right]^{1/2}\ . \tag{2.22}$$

If A is increased beyond $A_c^{(1)}$ (assuming the bound polaron remains of type-I character) the function $\mathscr{E}_{\rm I}(R)$ no longer has a minimum at a finite value of R. The only

possibility is a small bound polaron, with radius equal to a lattice constant. As A increases beyond $A_c^{(l)}$, the bound-state radius thus collapses.

The above remarks assume that the bound polaron always retains type-I character, and in practice this need not be the case. As the bound-state radius shrinks $|\psi_e(0)|^2$ increases, and near the center of the bound state $h(i)$ may become large enough to saturate the core. Then once again Emin-Holstein scaling breaks down. If we require A to be such that the core just saturates when $r_0=a_B/2$, and again employ the hydrogenic orbital, we find from Eq. (2.9) that saturation occurs when $A=A_c^{(s)}$, where

$$A_c^{(s)}=\left[1-\frac{H_0}{H_c}\right]\frac{\pi a_B^3 H_c}{4V_c} . \tag{2.23}$$

When $A_c^{(s)}>A_c^{(l)}$, then as A increases the bound magnetic polaron is always type I until the critical value $A_c^{(l)}$ is reached, after which the collapse described above will occur. This is equivalent to the situation described by Emin and Holstein. But in the opposite limit $A_c^{(l)}>A_c^{(s)}$, a different behavior is found. As A increases, r_0 decreases from a_B to a value $r_1>a_B/2$ where core saturation begins, and conclusions reached from the scaling argument break down. Further increases in A produce a more modest decrease in r_0 because the loss in kinetic energy is offset less efficiently by the increase in binding energy. A detailed calculation is required to explore this issue.

This concludes our discussion of the general properties of the ferron and the bound magnetic polaron. What remains is to explore the possibility that in three-dimensional antiferromagnets, type-II ferrons may exist, and also to explore the bound magnetic polaron with attention to the type-II region where $A_c^{(l)}>A_c^{(s)}$. We turn to this in Sec. III, with application to EuTe.[12]

III. EXPLICIT CALCULATIONS AND APPLICATIONS TO EuTe

We begin by exploring the properties of type-II ferrons within the framework of a variational calculation based on use of the hydrogenic $1s$ orbital:

$$\psi_{1s}(r)=\frac{1}{(\pi r_0^3)^{1/2}}\exp(-r/r_0) \tag{3.1}$$

with r_0 the variational parameter. With EuTe in mind, we consider a fcc lattice for which the volume V_c of the unit cell is $V_c=a^3/4$, where a is the lattice parameter. Then, if r_c is the radius of the saturated core, the number of spins N_c within the core is $N_c=(16\pi/3)(r_c/a)^3$.

The radius of the core is found from Eq. (2.10) and we have

$$\exp(-2r_c/r_0)=\frac{8\pi(H_c-H_0)}{A}\left[\frac{r_0}{a}\right]^3 \tag{3.2}$$

for any choice of r_0.

With the hydrogenic orbital, the right-hand side of Eq. (2.16) (with $\langle V\rangle=0$) may be evaluated in closed form:

$$\mathscr{E}_{\rm II}=\frac{\hbar^2}{2m^*r_0^2}+\frac{8\pi}{3}\left[\frac{r_c}{a}\right]^3 H_c S\left[1-\frac{H_0}{H_c}\right]^2-\tfrac{1}{2}AS\left[1-\frac{H_0}{H_c}\right]\left\{1-\left[1+2\frac{r_c}{r_0}+2\left[\frac{r_c}{r_0}\right]^2\right]\exp(-2r_c/r_0)\right\}$$
$$-\frac{A^2S}{256\pi H_c}\frac{1}{r_0^3}\left[1+4\frac{r_c}{r_0}+8\left[\frac{r_c}{r_0}\right]^2\right]\exp(-4r_c/r_0) . \tag{3.3}$$

Some useful dimensionless parameters are $\lambda=(1-H_0/H_c)$, $b_c=(8\pi H_c\lambda/A)^{1/3}$, $d=(2m^*a^2AS\lambda/\hbar^2b_c^2)$, $R'=(r_0/a)b_c$, and for the energy we use as a dimensionless measure $\epsilon=(2m^*a^2\mathscr{E}_{\rm II}/\hbar^2b_c^2)$. We may then regard R as the variational parameter, and if $R\le 1$ we have after some algebra in Eq. (3.3)

$$\epsilon(R')=\frac{1}{R'^2}-\frac{d}{2}+\tfrac{3}{16}dR'^3[\tfrac{5}{7}-7\ln R'+9(\ln R')^2$$
$$-6\ln(R')^3] . \tag{3.4}$$

In these units Eq. (3.2) becomes $\exp(-2r_c/r_0)\equiv R'$, and the constraint $R'<1$ confines our attention to the type-II ferron with saturated core.

At this stage we see clearly the effect of the saturation of the magnetization, implying that the Emin-Holstein scaling prediction $E(R)\to-\infty$ as $R\to 0$ breaks down, as noticed earlier. Since the scaling length of the problem is r_0, to which R' is proportional, the limit $R\to 0$ amounts to taking the limit $R'\to 0$ in Eq. (3.4). Since the spin polarization along $\hat{\mathbf{z}}$ cannot diverge but can only saturate to unity, the deformation energy of the system Ξ does not diverge at $R=0$ but saturates to a value which contributes $-d/2$ in Eq. (3.4). Then only the kinetic energy diverges [term $1/R'^2$ in Eq. (3.4)] implying that $\epsilon\to+\infty$ as $R,R'\to 0$.

The parameter d now provides a dimensionless measure of the strength of the local-moment—conduction-electron exchange. The variations of ϵ as a function of R' are illustrated in Fig. 2 for several values of d. We find the condition for a minimum in $\epsilon(R)$ at negative energy is

$$d\ge 21.86 , \tag{3.5}$$

and from this result we can obtain an estimate of the critical value A_c of the exchange parameter A above which the ferron is stable:

$$A_c=\left[\frac{21.86\hbar^2}{2m^*a^2S}\right]^{3/5}(8\pi H_c)^{2/5}\left[\frac{H_c}{H_c-H_0}\right]^{1/3} . \tag{3.6}$$

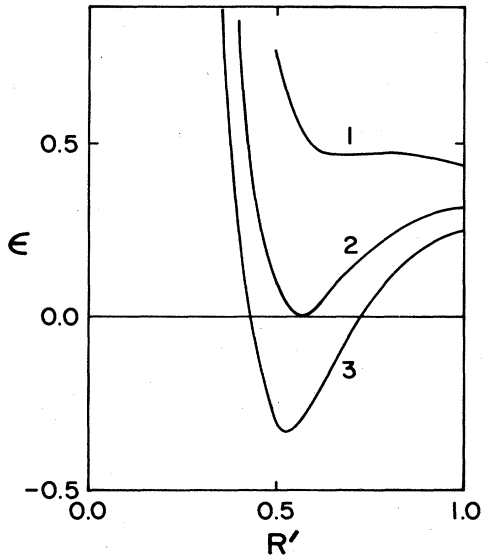

FIG. 2. The reduced energy of the type-II ferron, as a function of the variational parameter R', which necessarily lies in the range $0<R'<1$. The curves are calculated for various values of the dimensionless coupling strength d: $d=18$ (curve 1), $d=21.85$ (curve 2), and $d=24$ (curve 3).

When $A=A_c$, we have the minimum at $R'=0.565$, so the radius of the ferron is $r_0=r_0^{(c)}$, where

$$r_0^{(c)}=0.565a\left[\frac{A_c}{8\pi H_c\lambda}\right]^{1/3}$$

$$=0.48a\left[\frac{\hbar^2}{m^*a^2SH_c}\right]^{1/5}\left[\frac{H_c}{H_c-H_0}\right]^{2/3}. \quad (3.7)$$

With these results in hand, we next turn our attention to the properties of EuTe, which is the only material in which ferrons have been conjectured to exist. For this crystal, $S=\frac{7}{2}$, and the Eu^{2+} ions are S-state ions. The Néel temperature $T_N=9.6$ K is affected only slightly by doping with small concentrations of donor impurities. But the magnetization curves $M(H)$ are influenced dramatically[8,13] by such doping, when $T<T_N$. In particular, a ferromagnetic component M_0 is superimposed on the magnetization curve of the pure antiferromagnet. Vitins and Wachter assume the origin of M_0 is due to ferrons, and write

$$M_0=nM_F\ , \quad (3.8)$$

where n is the concentration of ferrons and M_F the magnetization associated with one isolated ferron. This assumes the ferrons do not interact. Two samples with different donor concentration N_d have been investigated in Ref. 8, but the authors note that interactions between the ferromagnetic entities are important in the more heavily doped sample. Attention has thus been focused on sample 399, for which N_D is believed small enough to make Eq. (3.8) valid. Since the ferron carries an electric charge, n is also the electron concentration deduced from transport measurements. From measured values of M_0 and n, Vitins and Wachter deduce that $M_F=14\,000\mu_B$, corresponding to clusters which contain 2000 Eu^{2+} ions. Of course, this requires the radius r_0 of the ferron to be very large.

In EuTe, $a=6.6$ Å. The field H_c at which the transition from the spin flop to the fully aligned ferromagnetic state is, for the bulk material, 7.5 T at low temperature.[13] When this is converted to energy units, recalling that we have set the gyromagnetic ratio equal to unity and used $2\mu_B$ (the electron moment) as the scale for magnetization, we have $H_c=0.86$ meV. If m_0 is the free electron mass, $m^*=0.4m_0$.[8] With $S=\frac{7}{2}$ and $H_0\ll H_c$, Eq. (3.7) gives $r_0^{(c)}=7.4$ Å, not far from the lattice constant. Therefore, unless A exceeds A_c by a very large amount (this is not the case), any ferrons present in this material will have a rather small radius, and will be unable to provide the large moment required to account for the data. The variational calculation upon which the above estimates are based could be improved, but in our view it is unlikely that an improved version would remove the very large discrepancy between the model predictions and the value of M_F inferred from the data. Moreover, from Eq. (3.6) again with $H_0\ll H_c$, we estimate $A_c=0.26$ eV actually larger than the value 0.15 eV deduced from magnetoreflectivity[14] and Faraday rotation[15] data implying that the ferron should be unstable in EuTe.

It is natural to inquire if electrons bound to donors (bound magnetic polarons) in a material such as EuTe can account for the data. In fact, at low temperature nearly all the electrons are frozen out on donor sites, so the moment required for each bound electron will clearly be very much smaller than that required for the hypothetical ferron. In EuTe the donor sites are associated with either iodine impurities or tellurium vacancies. In EuTe the Bohr radius is not large. One has $\epsilon_0=8$ for the dielectric constant,[16] so the Bohr radius $a_B=\epsilon_0\hbar^2/m^*e^2=10.6$ Å. If we use this as an estimate for r_0 in $R'=r_0b_c/a$, and choose $A=0.15$ eV, then R' is smaller than unity even in the absence of an external field. The core of the bound magnetic polaron in EuTe is thus expected to be saturated.

We have calculated, again with the hydrogenic $1s$ wave function as the variational function, the energy of the bound magnetic polaron as a function of R, given by

$$\epsilon(R')=(R')^{-2}-\frac{d}{2}+\tfrac{3}{16}dR'^3[\tfrac{5}{7}-7\ln R'+9(\ln R')^2-6(\ln R')^3]-2a/(a_Bb_cR')$$

with the last term, added to Eq. (3.4), representing the Coulomb potential. The results are displayed in Fig. 3 for the parameters given above and compared with the analogous curve calculated for the simple hydrogenic level with $A=0$. Note how the orbital radius has shrunk, consistent with the qualitative discussion of Sec. II. The minimum in the energy occurs now at $r_0=6.72$ Å, and we find $r_c=0.994r_0=6.7$ Å.

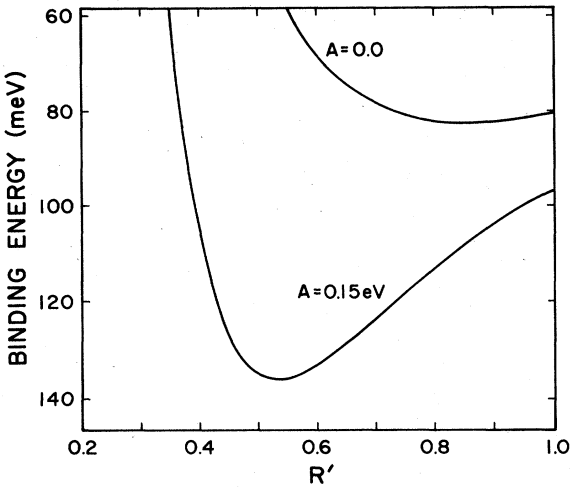

FIG. 3. Energy of the bound magnetic polaron in EuTe, as a function of the variational parameter R', related to the radius r_0 of the variational wave function by the relation r_0 (Å)$=12.5R'$ (curve labeled 0.15 eV). The curve labeled $A=0$ is that appropriate to the simple hydrogenic impurity, for comparison. The calculations are for zero applied field.

The magnetization of the bound magnetic polaron may be written

$$M_{\rm bmp}=2S\mu_B\left[N_c+\int\frac{d^3r}{V_0}\left[\sin\theta(r)-\frac{H_0}{H_c}\right]\right]$$
$$=2S\mu_B\left[N_c+\frac{A}{2H_c}\int_{r>r_c}d^3r\,|\psi_c(r)|^2\right], \quad (3.9)$$

and the anomalous contribution to the magnetization is then $N_D M_{\rm bmp}$, if we associate this with bound magnetic polarons.

At low temperatures one may evaluate N_D by relating it to the free-carrier concentration n through the relation $n=N_D\exp(-E_A/k_BT)$, with E_A the activation energy deduced from transport measurements. Vitins and Wachter have determined $n=4\times10^{18}$ cm^{-3}, $E_A=0.022$ eV at $T=300$ K, so one has $N_D\cong9\times10^{18}$ cm^{-3}. For $H_0/H_c\ll1$, when the contribution from the background material is added to that in Eq. (3.9), the relation between the magnetization M and the Zeeman field H_0 has the form

$$M=M_0+\chi H_0\ , \quad (3.10)$$

where $M_0=N_D M_{\rm bmp}$ is independent of the field H_0, and $\chi_0=2S\mu_B N/H_c$ is the magnetic susceptibility of pure EuTe. In Fig. 4, we compare the prediction of the form in Eq. (3.10) with the data.[17]

The calculation shows each bound magnetic polaron contributes $545\mu_B$ to the anomalous magnetization. This is equivalent to the contribution from the moment of roughly 75 Eu spins. The saturated core contains roughly 20 spins, so roughly 70% of the moment associated with the bound magnetic polaron comes from the halo around the core, where the conduction-electron—local-moment

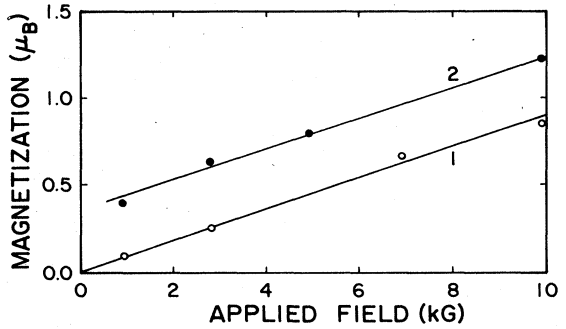

FIG. 4. Magnetization curve of EuTe for a pure sample (curve 1) and doped sample 399 (curve 2); the data are reported in Ref. 8, and the solid lines display the field variation expected from the bound magnetic polaron picture.

exchange enhances the contribution from the canted spin array. We then find an additional contribution to the moment of $0.36\mu_B$ per unit cell, which is in good accord with the data.

The calculations reported above apply specifically to EuTe. In principle, bound magnetic polarons of the sort described here may influence the properties of many materials. We conclude with a "phase diagram," constructed with the simple hydrogenic function as the basis for a variational calculation which outlines the regimes within which one has a saturated core (type-II bound magnetic polaron) or an unsaturated core (type-I). We show this in Fig. 5; as A is increased with the ratio of the two initial values $A_c^{(s)}$ and $A_c^{(l)}$ held fixed, when one crosses the solid line in Fig. 5, there is a sudden collapse of the bound state from a "large" to a "small" state. As one crosses the

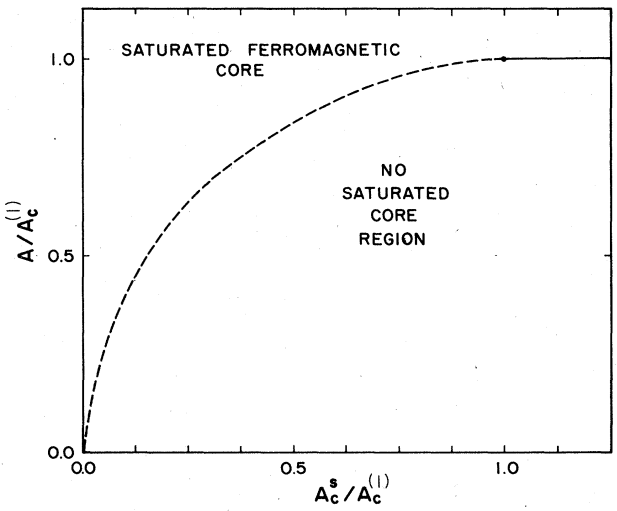

FIG. 5. A phase diagram for the bound magnetic polaron, as a function of A, deduced as described in Sec. III. With increasing A, when $(A_c^{(s)}/A_c^{(l)})>1$, there is a sudden collapse of the state from "large" to a "small" bound magnetic polaron as the solid line is crossed. When $(A_c^{(s)}/A_c^{(l)})<1$, the core saturates as one crosses the dashed line, but there is no discontinuous change in the character of the state.

dashed line where $(A_c^{(s)}/A_c^{(l)})<1$, core saturation sets in in a gradual and smooth fashion.

IV. CONCLUDING REMARKS

Until now, EuTe has been the only material within which it has been argued[1,13] that experimental evidence for ferrons exists. As we have seen, the present study concludes that these entities in fact are not stable, and instead, bound magnetic polarons with their large induced ferromagnetic moment are responsible for the anomalous contribution to the magnetization measured in doped EuTe. It is perhaps worthwhile to comment in a bit more detail on our choice of parameters and the relationship of the present theoretical study to earlier work.

First of all, the electron effective mass m^* has been inferred by more than one method in Ref. 8. Also, H_c, the field at which the transition from the spin flop to the fully aligned state occurs in bulk material, has been measured directly, as noted earlier.[13] In our numerical applications, our value $A=0.15$ eV has been justified by measurements of the splitting of Faraday rotation and peaks in EuTe, giving $\frac{1}{2}AS=0.27$ eV. The study of the red shift of the absorption edge in the ferromagnet EuO provides the value $\frac{1}{2}AS=0.27$ eV[1], and tunneling transport experiments give $\frac{1}{2}AS=0.24$ eV for the ferromagnet EuS. Since the value of A should be quite similar for all the europium chalcogenides, our choice should not be that far off.

We may also compare our results with the previous study of this state by previous workers, most particularly those by Umehara and his colleagues.[6,19] Their results are summarized in Fig. 4 of Ref. 6. These calculations assume a tight-binding model for the conduction electrons, allow for an admixture of spin-down as well as spin-up character in the electron wave function, and then solve the resulting self-consistent equations of the model without use of the hydrogenic variational function. We include the finite magnetic field, and view our discussion as providing useful insights into the ferron problem, but one can inquire if there are appreciable quantitative differences between the two studies. In the notation of Ref. 6, IS corresponds to our $\frac{1}{2}AS$, optical experiments show the conduction-electron bandwidth (E_0 in Ref. 6) to be 2.5 eV, and $JS^2=75\times10^{-5}$ eV. Then, in reference to Fig. 4 of Ref. 6, $E_0/IS=9.25$, while $JS^2/IS=0.0029$, and the conclusion of the earlier studies is also that the ferron is unstable.

Recently, Umehara[19] has argued that electron-phonon interactions may stabilize the ferron, but still finds that for $E_0\geq2$ eV (note earlier we refer to the conduction-electron bandwidth as W) the ferron remains unstable in EuTe. He also investigated the cases $E_0=1$ eV and 1.5 eV, with $IS=0.35$, parameters we view as unrealistic for this material. If we assume, in our picture, that m^* scales inversely with bandwidth, the value $A=0.2$ eV, deduced from Umehara's choice of IS, leads also to a stable ferron, and to conclusions compatible with Fig. 4 of Ref. 6 (which also indicates a stable ferron). The point of the remarks in this paragraph is that our calculation leads to the same conclusions on the stability of the ferron as the earlier works.

Note finally that, in contrast to pictures advanced elsewhere, our calculation shows that the dominant contribution to the magnetic moment of the bound magnetic polaron comes not from the ferromagnetic core, which we find is indeed present, but instead from the halo which surrounds this core within which the ferromagnetic moment is enhanced over that in the bulk material far from the donor site. Also, the bound state is quite compact, to judge by the value of r_0 we find, which is substantially smaller than the Bohr radius (10.6 Å) of the "bare" donor level in this material. The physical picture we offer thus differs considerably from that discussed by earlier authors.

Finally, the existence of ferrons in three-dimensional systems is unlikely since it requires large values of A. Therefore, if any ferron is to be observed, it is presumably in one-dimensional antiferromagnetic semiconductors. Indeed, our model predicts their existence, but some approximations we have made, valid in three dimensions, become questionable in one dimension: We have neglected zero-point spin fluctuations by treating the local moments classically. It is known, however, that such fluctuations are strong enough to destroy the one-dimensional antiferromagnetic ordering. Such an ordering is made possible either by an anisotropy field or by small "interchain" interactions. Both of them have been neglected in our model. Therefore, a quantum-mechanical treatment of the spin assembly including anisotropy fields is required before any definite conclusion is drawn on ferrons in antiferromagnetic chains.

ACKNOWLEDGMENT

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[17]In the limit of low magnetic fields H_0, Eq. (3.10) must be corrected to take into account the demagnetization factor N_d so that $M=\chi_0 H_0+H_0/N_d$ if $H_0 \leq N_d M$. This part of the magnetization curve does not present any interest for our purpose which is to derive general conclusions on EuTe, since N_d depends on the geometrical shape of the particular samples investigated. We then only study the magnetization curve for fields $H_0 \geq N_d M$ where Eq. (3.10) applies.

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