Thermoelectric power of small polarons in magnetic semiconductors

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The thermoelectric power (Seebeck coefficient) α of a small polaron in both ferromagnetic and antiferromagnetic semiconductors and insulators is calculated for the first time. In particular, we obtain the contribution to the Seebeck coefficient arising from exchange interactions between the severely localized carrier (i.e., small polaron) of charge q and the spins of the host lattice. In essence, we study the heat transported along with a carrier. This heat, the Peltier heat, Π, is related to the Seebeck coefficient by the Kelvin relation: $\Pi=qT\alpha$, where T is the temperature. The heat per carrier is simply the product of the temperature and the change of the entropy of the system when a small polaron is added to it. The magnetic contribution to the Seebeck coefficient is therefore directly related to the change of the magnetic entropy of the system upon introduction of a charge carrier. We explicitly treat the intrasite and intersite exchange interactions between a small polaron and the spins of a spin-$\frac{1}{2}$ system. These magnetic interactions produce two competing contributions to the Seebeck coefficient. First, adding the carrier tends to provide extra spin freedom (e.g., spin up or spin down of the carrier). This effect augments the entropy of the system, thereby producing a positive contribution to the Peltier heat. Second, however, the additional exchange between the carrier and the sites about it enhances the exchange binding among these sites. This generally reduces the energetically allowable spin configurations. The concomitant reduction of the system's entropy provides a negative contribution to the Peltier heat. At the highest of temperatures, when kT exceeds the intrasite exchange energy, the first effect dominates. Then, the Peltier heat is simply augmented by $kT\ln 2$. Alternatively, at temperatures well below the magnetic transition temperature, the second effect dominates. The Peltier heat then garners a negative contribution. In the experimentally accessible range between these limits, both effects are comparable. There the magnetic contribution to the Seebeck coefficient is generally sizable, $\sim 100\ \mu$V/K. Furthermore, this magnetic contribution to the Seebeck coefficient is distinguished from the usual nonmagnetic contribution by its temperature dependence; it rises with temperature. Thus, the exchange interactions between a small polaron and its magnetic environment produce a significant and distinctive contribution to the carrier's Seebeck coefficient.

I. INTRODUCTION

The thermoelectric power (Seebeck coefficient) α is the average entropy per unit charge, q, transported along with a charge carrier.[1] In the absence of energy flow associated with the specific transport process (e.g., phonon drag for itinerant motion[2] and vibrational energy transported in a jump for hopping motion[3,4]), the basic quantity can be calculated from thermodynamics. Namely, one computes the change of the entropy of the system when a carrier is added to it. This amount of entropy is transported with the carrier as it passes through the material. For free carriers, the Seebeck coefficient associated with carriers of energy ϵ, $\alpha(\epsilon)$, is simply $|\epsilon-\mu|/qT$, where T is the temperature and μ is the chemical potential. The net Seebeck coefficient α is then the average of this quantity weighted by the partial conductivity attributed to carriers of energy ϵ, $\sigma(\epsilon)$, and

$$\alpha=\int \alpha(\epsilon)\sigma(\epsilon)d\epsilon \Big/ \int \sigma(\epsilon)d\epsilon\ .$$

For convenience, we discuss the energy corresponding to the Seebeck coefficient: the Peltier heat, $\Pi\equiv qT\alpha$. For free carriers of energy ϵ, $\Pi=|\epsilon-\mu|$. However, the situation becomes more complex when one explicitly considers the interactions of the carriers with one another or with the atoms of the solid. For example, the free-carrier formula is altered by that interaction of the carrier with the lattice that is responsible for the shift of the energy levels of an insulator with temperature.[5,6] In magnetic semiconductors, in addition to the electron-lattice interaction, the carrier interacts with the solid via exchange interactions. Here we consider the effect of these magnetic interactions on the Peltier heat of a severely localized carrier (i.e., small polaron) in a magnetic semiconductor.

Small-polaron formation occurs when a carrier is bound in the potential well produced by shifts of the equilibrium

positions of the atoms surrounding the carrier. These (trapping) atomic displacements are themselves stabilized by the carrier's occupation of this potential well. Such "self-trapping" is a result of the carrier's electron-lattice interaction. When small-polaron formation occurs in a magnetic solid (e.g., MnO) the self-trapped carrier also interacts with the magnetic moments of the solid via exchange interactions. In this paper we study the effect of these interactions on the Seebeck coefficient (Peltier heat) of a small polaron. For simplicity, we ignore the modifications of our calculations arising from the dependences of the exchange energies on atomic displacements (the magnon-phonon interaction). This is consistent with our purpose: understanding the basic effect of exchange interactions on the small polaron's Seebeck coefficient. In small-polaron hopping a charge remains localized on an atomic site for a long time ($\gg 10^{-12}$ sec) and only makes occasional rapid jumps between adjacent atomic sites. Thus, the magnetic interactions of a small polaron are those of a charge carrier confined to a single atomic site. As such, the results of this paper are not directly applicable to band transport or to shallow-impurity conduction where the presumption of such severe localization is inappropriate. Nonetheless, the general method of this paper can be applied to the calculation of the Peltier heat of an itinerant carrier.[5,6] In particular, the Peltier heat of an itinerant carrier is found by computing the change of the entropy of the system when a carrier is added to a state of quasimomentum $\vec{k}$.

The effect of spin on the Peltier heat of a small polaron in a magnetic semiconductor has been considered before. In particular, Heikes *et al.*[7,8] introduced the term

$$\Pi_{\rm mag}=kT\ln\frac{2S+1}{2S_0+1}$$

for the magnetic contribution to Peltier heat above the magnetic transition temperature, in the paramagnetic regime. Here S and S_0 denote, respectively, the net spin of a magnetic site with and without the presence of the carrier spin at the site. We show that in the paramagnetic regime, in addition to this spin-degeneracy contribution, there is another term of comparable magnitude and opposite sign. It originates from the exchange between the carrier and the surrounding magnetic sites. This result represents just one regime of a general calculation of the magnetic contribution to a small polaron's Peltier heat. We also consider the magnetic effect in the low-temperature magnetically ordered state.

To calculate the Peltier heat Π we compute the product of the temperature and change in entropy of a system of n carriers on N sites upon adding an additional carrier:

$$\Pi=-T\frac{\partial}{\partial T}(F^{n+1}-F^n)\ . \tag{1}$$

Here F^n denotes the free energy of a system with n carriers. Ignoring interactions among the carriers themselves, as is appropriate for low carrier concentrations ($c\equiv n/N\ll 1$), the above expression reduces to

$$\Pi=-T\frac{\partial}{\partial T}(F^1-F^0)+kT\ln[(1-c)/c]\ . \tag{2}$$

The final term on the right-hand side is simply of combinatorial origin. It is the change of the entropy of a distribution of particles among N equivalent sites when the particle number is increased from n to $n+1$. Using the Fermi relation

$$c=\{\exp[(\epsilon-\mu)/kT]+1\}^{-1}\ ,$$

this term may be rewritten as $\epsilon-\mu$. The first term on the right-hand side,

$$-T\frac{\partial}{\partial T}(F^1-F^0)\equiv\Pi_{\rm mag}\ , \tag{3}$$

is the contribution to the Peltier heat due to the magnetic nature of the carrier and the host lattice. For example, in the absence of interactions when the carrier has equal probability of having its spin up or down, $\Pi_{\rm mag}$ is simply $kT\ln 2$. Our purpose here is to calculate $\Pi_{\rm mag}$ in the presence of spin interactions between the carrier and the magnetic host atoms. We consider temperatures both below and above the magnetic transition temperature.

We shall first consider a one-dimensional chain of spin-$\frac{1}{2}$ sites and calculate the change in entropy resulting from adding a carrier to this system. Two models of the carrier-host exchange interaction are treated. (A) To begin, we consider a mean-field treatment in which all spins interact by Ising exchange. (B) Next, we extend the model so that the intrasite coupling of the carrier to the occupied site is via Heisenberg exchange and the intersite coupling is via Ising exchange. Here the mean-field approximation is only applied to sites which are neither occupied nor nearest neighbors of the carrier. Finally, we extend the idea used in model B to a simple-cubic lattice. The expressions for the Peltier heat derived from different models contain the same qualitative features. Namely, below the magnetic ordering temperature, $\Pi_{\rm mag}$ is small and negative. At temperatures between the transition temperature and the temperature corresponding to intrasite exchange (typically $\sim 10^4$ K), $\Pi_{\rm mag}$ is the sum of a negative term associated with the intersite exchange and the positive (Heikes) contribution which arises from spin degeneracy (except for model A as we subsequently show). Significant cancellations can occur between these terms because they are of comparable magnitude. Finally, at the highest of temperatures, above that associated with intrasite exchange, $\Pi_{\rm mag}$ is simply $kT\ln 2$. This corresponds to all spin states being equally occupied. It should also be pointed out that our results are independent of the sign of the intersite exchange. That is, they apply to both ferromagnets and antiferromagnets. This is because it is only the degree of canting of the spins about the carrier that changes the free energy.

In the following sections we first present calculations of $\Pi_{\rm mag}$ for a one-dimensional chain of magnetic sites. We then generalize our formulation to a three-dimensional crystal where the magnetic sites comprise a simple-cubic lattice. The paper concludes with a synopsis and discussion of our work.

II. CALCULATION OF Π_{mag} FOR A ONE-DIMENSIONAL CHAIN

A. Ising model in the mean-field approximation

Consider an Ising model of a one-dimensional ferromagnetic closed chain of N spin-$\frac{1}{2}$ magnetic sites with nearest-neighbor exchange. In the absence of a carrier, the Ising exchange Hamiltonian is

$$\mathscr{H}^0=-J\sum_{i=1}^{N}\sigma_i\sigma_{i+1}\ , \tag{4}$$

where J denotes the exchange integral between adjacent spins, σ_i at site i and σ_{i+1} at site $i+1$. The Ising spin takes the value $\sigma_i=\pm1$ with $\sigma_{N+1}=\sigma_1$. We rewrite $\mathscr{H}^0$ as

$$\mathscr{H}^0=-\tfrac{1}{2}\sum_{i,j}J_{i,j}(\sigma_i-\mathscr{S})(\sigma_j-\mathscr{S}) +\frac{\mathscr{S}^2}{2}\sum_{i,j}J_{i,j}-\frac{\mathscr{S}}{2}\sum_{i,j}J_{i,j}(\sigma_i+\sigma_j)\ , \tag{5}$$

where $\mathscr{S}$ is the thermal average of a spin; it is independent of the site index i. In the mean-field (MF) approximation, the first term on the right-hand side, representing spin fluctuations, is neglected. The remaining two terms yield

$$\mathscr{H}^0_{\rm MF}=NJ\mathscr{S}^2-2J\mathscr{S}\sum_{j=1}^{N}\sigma_j\ .$$

The corresponding free energy is

$$F^0=-kT\ln Z^0_{\rm MF}\ ,$$

where the partition function $Z^0_{\rm MF}$ is

$$Z^0_{\rm MF}={\rm Tr}\,e^{-\mathscr{H}^0\beta} =e^{-NJ\mathscr{S}^2\beta}\sum_{\{\sigma_1,\ldots,\sigma_N\}}\exp\left[2J\sum_j\sigma_j\beta\right]\ ,$$

and $\beta\equiv1/kT$. It is straightforward to carry out the summation over all the spin configurations in $Z^0_{\rm MF}$:

$$Z^0_{\rm MF}=e^{-NJ\mathscr{S}^2\beta}\prod_{j=1}^{N}\sum_{\sigma_j=\pm1}\exp(2J\mathscr{S}\sigma_j\beta) =e^{-NJ\mathscr{S}^2\beta}[2\cosh(2J\mathscr{S}\beta)]^N$$

and

$$F^0=NJ\mathscr{S}^2-NkT\ln[2\cosh(2J\mathscr{S}\beta)]\ . \tag{6}$$

We now introduce a carrier with Ising spin σ_0 at site n to the above-described carrier-free magnetic system. Again considering only nearest-neighbor exchange, the corresponding Hamiltonian is

$$\mathscr{H}^1=-J\sum_{j=1}^{N}\sigma_j\sigma_{j+1}-J(\sigma_0\sigma_{n-1}+\sigma_0\sigma_{n+1})-J_0\sigma_0\sigma_n\ , \tag{7}$$

where J_0, taken to be positive, is the intrasite exchange integral linking the carrier spin σ_0 with the spin of the occupied site, σ_n. The coupling strength between the carrier spin and its two nearest neighbors, $\sigma_{n\pm1}$, for simplicity, is taken to be the same as that between σ_n and $\sigma_{n\pm1}$, namely J.

We again introduce the mean-field approximation for the intersite exchange, but treat the intrasite coupling exactly within the Ising model. To begin, we note that the thermal averages of the carrier spin σ_0 and the host spin at the same site, σ_n, share a common value, S_0:

$$\langle\sigma_0\rangle=\langle\sigma_n\rangle=S_0\ . \tag{8a}$$

Similarly, by symmetry the thermal average of the two spins adjacent to the occupied site, σ_{n-1} and σ_{n+1}, equal one another,

$$\langle\sigma_{n-1}\rangle=\langle\sigma_{n+1}\rangle=S_1\ . \tag{8b}$$

As a zeroth-order approximation, the next-nearest and higher-order neighbors of the carrier, which are not directly coupled to the carrier, are presumed to have a common thermal average denoted by S,

$$\langle\sigma_i\rangle=S\quad\text{for } i\neq0,n,n\pm1\ . \tag{8c}$$

That is, the presence of the carrier is taken to affect only the occupied site and its neighbors. Employing the mean-field approximation and neglecting spin fluctuations about the average spins S_0, S_1, and S of Eqs. (8a)–(8c) reduces the Hamiltonian for the Ising ring with a spin added at site n to

$$\mathscr{H}^1_{\rm MF}=(N-4)S^2J+2J(2S_0+S)S_1-\sum_{i=0}^{N}H_i\sigma_i-J_0\sigma_0\sigma_n\ . \tag{9}$$

Here the effective intersite exchange field acting on spin σ_i, namely H_i, is

$$\begin{aligned}&H_0=H_n=2JS_1\ ,\\ &H_{n\pm1}=J(S+2S_0)\ ,\\ &H_{n\pm2}=J(S+S_1)\ ,\\ &H_j=2JS,\quad j=1,2,\ldots,n-3,n+3,\ldots,N\ .\end{aligned} \tag{10}$$

Using Eqs. (9) and (10) we obtain the free energy in the presence of a carrier,

$$F^1=(N-4)S^2J+2J(2S_0+S)S_1-kT(N-1)\ln2-kT(N-5)\ln[\cosh(2JS\beta)]-2kT\ln\{\cosh[J(S+S_1)\beta]\} -2kT\ln\{\cosh[J(S+2S_0)\beta]\}-kT\ln(2\{\cosh[(2JS_1+J_0)\beta]\}\exp(2JS_1\beta)+2\{\cosh[(2JS_1-J_0)\beta]\}\exp(-2JS_1\beta))\ . \tag{11}$$

The magnetic contribution to the Peltier heat can be readily calculated by substituting Eqs. (11) and (6) into Eq. (3). Foregoing the complicated algebra, we present the main features of Π_{mag} for the following limiting cases.

1. *Paramagnetic regime:* $T > T_c$

Above the transition temperature $T_c = 2J/k$ (appropriate to a ferromagnetic linear chain) the thermal averages of the spins vanish. The change in free energy upon adding a carrier is then simply

$$F^1 - F^0 = -kT \ln[2\cosh(J_0\beta)] . \tag{12}$$

Employing Eq. (3) with Eq. (12) then yields the magnetic contribution to the Peltier heat,

$$\Pi_{mag} = kT \ln 2 + kT \ln[\cosh(J_0\beta)] - J_0 \tanh(J_0\beta) . \tag{13}$$

The magnitude of the corresponding magnetic contribution to the Seebeck coefficient, $\Pi_{mag}/|q|T$, is plotted in Fig. 1. The intersite exchange J is not contained in Eqs. (12) and (13). This is because we have subjected each site to the mean-field approximation. Our subsequent discussion transcends this oversimplification. It is now instructive to examine two limits of Eq. (13).

(a) $T \gg J_0/k$. At extremely high temperature, i.e., $T \gg J_0/k$ ($\gg T_c$), Eq. (13) is dominated by the first term on its right-hand side,

$$\Pi_{mag} \simeq kT \ln 2, \quad T \gg J_0/k . \tag{14}$$

This result corresponds to the interaction of the carrier with the magnetic host being insignificant. In particular, for $T \gg J_0/k$ Hund's-rule and non-Hund's-rule states are equally occupied. Hence the change in entropy on adding an electron to a spin-$\frac{1}{2}$ system arises solely from the twofold degeneracy of the carrier.

(b) $J_0/k \gg T > T_c$. At temperatures above T_c but much less than the intrasite exchange we expand the second and third terms of Eq. (13) for large values of $J_0\beta$. This leads to a very small positive magnetic contribution to the Peltier heat which depends only on the *intrasite* exchange and the temperature,

$$\Pi_{mag} \simeq 2J_0 e^{-2J_0\beta}, \quad J_0/k \gg T > T_c . \tag{15}$$

We note that the Heikes spin-degeneracy term ($kT \ln \frac{3}{2}$) does not appear in Eq. (15) despite the fact that for $T \ll J_0/k$ the spin of the added electron lines up with the host spin. This is an artifact of the Ising model. Within the Ising model the degree of spin degeneracy at the occupied site is unaltered by the presence of the carrier. However, as we subsequently show, this is not true with Heisenberg exchange.

2. *Ordered regime:* $T \ll T_c$

At temperatures well below the transition temperature, the thermal average of the spins in the presence of a carrier approaches that of the carrier-free case, i.e., $S_0 \simeq S_1 \simeq S \simeq \mathcal{S}$.[9] There the thermal averages of the spins reach their common temperature-independent saturation value. In this limit Eqs. (3), (6), and (11) yield

$$\Pi_{mag} = -12J e^{-4J\mathcal{S}\beta}, \quad T \ll T_c . \tag{16}$$

The small negative value of Π_{mag} is a general feature of the low-temperature regime. It occurs because the added exchange interactions associated with the added spin cause an increased fanning out of the system's magnetic energy levels. Thus the occupation of excited energy levels, which is a measure of the system's entropy, is reduced when the spin is added.

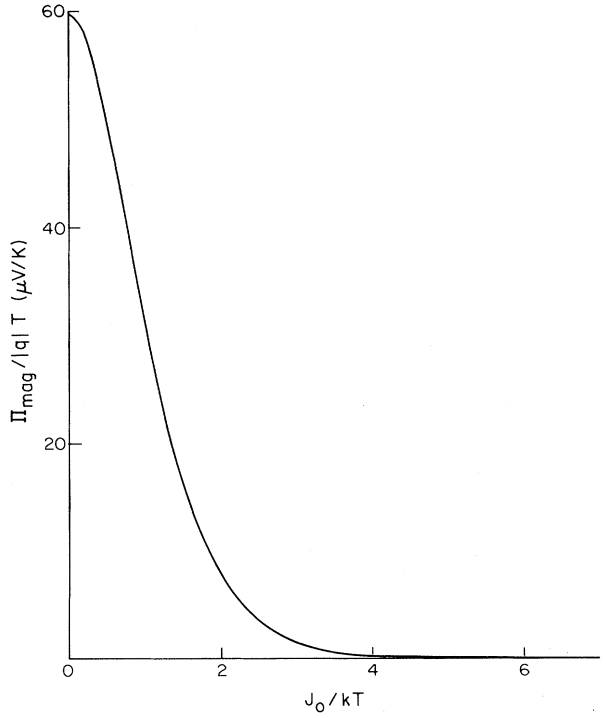

FIG. 1. Magnitude of the magnetic contribution to the Seebeck coefficient, $\Pi_{mag}/|q|T$, is plotted against J_0/kT in the paramagnetic regime for a one-dimensional Ising chain in the mean-field approximation.

B. Three-site cluster embedded in a mean-field magnet

In the preceding treatment we modeled the exchange interaction by the Ising Hamiltonian and then employed the mean-field approximation. We found that for $J_0/k \gg T > T_c$ neither the intersite exchange nor the correct spin degeneracy appear in Π_{mag}, Eq. (15). In order to investigate these features, we now treat the problem in a more realistic manner.

As before, we consider an Ising ring. However, we "rescue" the occupied site n and its neighbors $n-1$ and $n+1$ from the mean-field approximation. That is, we treat our system as a three-site cluster embedded in the effective field produced by the remaining spins. Without the carrier there are three spins on the three sites of the cluster. Adding a spin at site n increases the number of spins of the three-site cluster to four. The added spin has a Heisenberg *intrasite* exchange. However, its intersite exchange is treated on the same footing as the other intersite exchange, i.e., by the Ising model.

In the absence of a carrier the reduced Hamiltonian is

$$\mathcal{H}^0_{\rm MF}=(N-2)J\mathcal{S}^2-J\sigma_n(\sigma_{n-1}+\sigma_{n+1})-\sum_{i=1}^{N}H_i\sigma_i\ , \quad (17)$$

where $\mathcal{S}$ is the thermal average of spins outside the cluster ($\mathcal{S}=\langle\sigma_i\rangle$, $i\neq n$, $n\pm1$) and H_i is the effective field at site i:

$$H_i=\begin{cases}J\mathcal{S}, & i=n\pm1\\ 0, & i=n\\ 2J\mathcal{S}, & \text{all the other sites}\ .\end{cases} \quad (18)$$

The corresponding partition function is

$$Z^0=e^{-(N-2)J\mathcal{S}^2\beta}[2\cosh(2J\mathcal{S}\beta)]^{N-3}z^0\ , \quad (19)$$

where

$$z^0=4[1+\cosh(2J\mathcal{S}\beta)\cosh(2J\beta)] \quad (20)$$

is the partition function for the three sites of the cluster.

With a carrier of spin $\vec{s}_0$ at site n, we write the Hamiltonian in terms of site spin operators (e.g., $\vec{s}_i$) and their z components (e.g., $s_{i,z}$) instead of the z components of the Pauli spin matrices, the σ_i's where $s_{i,z}\equiv\sigma_i/2$. With this notation the Hamiltonian for the magnetic system with a carrier on site n is written as the sum of the Hamiltonian of the three-site, four-spin cluster, $\mathcal{H}_c$, and the reduced (effective-field) Hamiltonian for the remaining sites of the closed chain,

$$\mathcal{H}^1_{\rm MF}=\mathcal{H}_c+(N-2)JS^2-\sum_{\substack{i=1\\ i\neq n,n\pm1}}^{N}4JSs_{iz}\ , \quad (21)$$

where S is the thermal average of the spins outside the cluster. The cluster Hamiltonian $\mathcal{H}_c$ is

$$\mathcal{H}_c=-2(s_{n-1,z}+s_{n+1,z})JS$$
$$-4J(s_{0,z}+s_{n,z})(s_{n-1,z}+s_{n+1,z})-4J_0\vec{s}_0\cdot\vec{s}_n\ . \quad (22)$$

The three terms of the Hamiltonian are readily understood. First, the Ising spins at site $n\pm1$ ($s_{n\pm1,z}\equiv\sigma_{n\pm1}/2$) experience the mean field JS of their neighbors from outside the cluster. Second, these spins are coupled to the two spins at site n, $\vec{s}_0$ and $\vec{s}_n$, by Ising exchange. Finally, the coupling between the carrier and the host spin at site n is described by the Heisenberg exchange. Again, we take J_0 to be positive.

To calculate the partition function Z^1 in the presence of a carrier, we diagonalize the cluster Hamiltonian $\mathcal{H}_c$. The eigenfunctions of $\mathcal{H}_c$ are simply the products of the eigenfunctions of $\vec{s}_0+\vec{s}_n$ with those of $\vec{s}_{n-1}+\vec{s}_{n+1}$. Using these eigenfunctions, we find

$$Z^1=e^{-(N-2)JS^2\beta}[2\cosh(2JS\beta)]^{N-3}z^1\ , \quad (23)$$

where the cluster partition function z^1 is

$$z^1=4e^{J_0\beta}[1+\cosh(2JS\beta)\cosh(4J\beta)]$$
$$+4e^{-J_0\beta}[1+\cosh(2JS\beta)]\ . \quad (24)$$

With $\mathcal{S}$ equaling S, as before, the change in free energy upon adding an electron is just that of the cluster, namely

$$F^1-F^0=-kT\ln(z^1/z^0)\ . \quad (25)$$

Using Eqs. (3), (20), (24), and (25), we find $\Pi_{\rm mag}$. The magnitude of the corresponding magnetic contribution to the Seebeck coefficient, $\Pi_{\rm mag}/|q|T$, in the paramagnetic regime, is given by curve a of Fig. 2. In the three physically significant temperature regimes we have

$$\Pi_{\rm mag}=\begin{cases}kT\ln2, & T\gg J_0/k\\ kT\ln(\frac{3}{2})-5J^2/3kT, & J_0/k\gg T>T_c\\ -8J(S+1)e^{-2J(S+1)/kT}, & T_c\gg T\ .\end{cases} \quad (26)$$

At extremely high temperatures, i.e., $T\gg J_0/k$, the carrier-produced change of the spin degeneracy dominates all exchange effects. By adding an electron to site n, the spin degeneracy of the occupied site changes from two (corresponding to $\sigma_n=\pm1$) to four (corresponding to a triplet and a non-Hund's-rule singlet). This change contributes the dominant term, $kT\ln2$, to $\Pi_{\rm mag}$. At temperatures above T_c but much less than J_0/k, occupation of the non-Hund's-rule state becomes unimportant. Thus, in this case the spin degeneracy contributes $kT\ln\frac{3}{2}$ to $\Pi_{\rm mag}$. In addition, exchange between site n and sites $n+1$ and

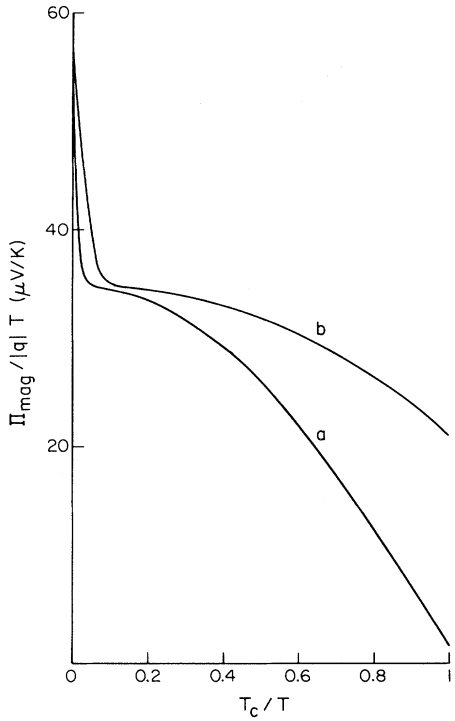

FIG. 2. Magnitude of the magnetic contribution to the Seebeck coefficient, $\Pi_{\rm mag}/|q|T$, in the paramagnetic regime is plotted against T_c/T. Curve a is for a three-site cluster embedded in a mean field in one dimension. The transition temperature T_c in the mean-field approximation is $2J/k$. Curve b is for a seven-site cluster embedded in a mean field in a simple-cubic lattice. The transition temperature T_c in the mean-field approximation is $6J/k$. For both curves a and b the ratio J_0/J is taken to be 100.

$n-1$ yields the term $-5J^2/3kT$. This originates from a decrease of the entropy of the spins of the cluster when a carrier is added. This spin-polarization effect is, of course, lost within the complete mean-field approximation because there intersite interaction vanishes for $T>T_c$; cf. Eq. (15). Finally, this spin-polarization effect yields the small negative value which dominates $\Pi_{\rm mag}$ at low temperatures, $T\ll T_c$. In this low-temperature regime this effect survives the mean-field approach. Specifically, at low temperatures with $\mathcal{S}\simeq S\simeq 1$, Eqs. (26) and (16) differ only in their numerical prefactors.

III. CALCULATION OF $\Pi_{\rm mag}$ FOR A SIMPLE-CUBIC LATTICE: SEVEN-SITE CLUSTER EMBEDDED IN A MEAN-FIELD MAGNET

To generalize our formulation to three dimensions we consider a seven-site cluster appropriate to a simple-cubic spin-$\frac{1}{2}$ lattice. The site to be occupied, $\underline{G}$, is the center of the cluster at (n,m,l), and $n\pm1$, $m\pm1$, and $l\pm1$ denote the six nearest-neighbor sites along the cubic directions. In the absence of a carrier the intersite exchange between the sites within the cluster is represented as Ising exchange. Interaction of the cluster with ions outside is approximated by the mean field $J\mathcal{S}$. Here, $\mathcal{S}$ again stands for the thermal average of the spins outside the cluster (the maximum value of $\mathcal{S}$ is chosen to be unity in order to be consistent with our prior definition of $\mathcal{S}$ in the one-dimensional case). In the absence of a carrier, the cluster partition function is given by

$$z^0=\sum_{\{\sigma_{\underline{g}}=\pm1\}}\exp\left[J\beta(\mathcal{S}+\sigma_{\underline{G}})\sum_{\underline{g}}\sigma_{\underline{g}}\right],$$

$$\underline{g}=n\pm1,m\pm1,l\pm1\ .$$

Carrying out the summations, we obtain

$$z^0=4[10+\cosh(6J\mathcal{S}\beta)\cosh(6J\beta)+6\cosh(4J\beta\mathcal{S})\cosh(4J\beta)+15\cosh(2J\mathcal{S}\beta)\cosh(2J\beta)]\ . \tag{27}$$

In the presence of a carrier spin $\vec{s}_0$ at site $\underline{G}$, the cluster now consists of eight spins. As in model B, we describe the intrasite coupling by the Heisenberg exchange, the nearest-neighbor coupling by the Ising exchange, and the exchange interaction involving sites outside the cluster by the mean field. The cluster Hamiltonian is diagonalized by using the product wave functions of the form $U_iV_jW_kX_l$, where U_i, V_j, W_k, and X_l each stand for one of the four eigenstates of $\vec{s}_0+\vec{s}_{\underline{G}}$, $\vec{s}_{n-1}+\vec{s}_{n+1}$, $\vec{s}_{m-1}+\vec{s}_{m+1}$, and $\vec{s}_{l-1}+\vec{s}_{l+1}$. Using the 2^8 eigenvalues (many of them are degenerate), we obtain the cluster partition function,

$$\begin{aligned}z^1=&\,2e^{J_0\beta}\{\cosh(6JS\beta)[1+2\cosh(12J\beta)]+6\cosh(4JS\beta)[1+2\cosh(8J\beta)]+15\cosh(2JS\beta)[1+2\cosh(4J\beta)]+30\}\\&+2e^{-3J_0\beta}[10+\cosh(6JS\beta)+6\cosh(4JS\beta)+15\cosh(2JS\beta)]\ .\end{aligned} \tag{28}$$

In a manner similar to our derivation of Eq. (26) for the one-dimensional case, we obtain $\Pi_{\rm mag}$ for our three-dimensional model. The magnitude of the corresponding magnetic contribution to the Seebeck coefficient, $\Pi_{\rm mag}/|q|T$, in the paramagnetic regime, is given by curve b of Fig. 2. Simple analytic expressions for three temperature regimes are

$$\Pi_{\rm mag}=\begin{cases}kT\ln2, & T\gg J_0/k\\ kT\ln(\frac{3}{2})-5J^2/kT, & J_0/k\gg T>T_c\\ -12J(S+1)e^{-2J(S+1)/kT}, & T_c\gg T\ .\end{cases} \tag{29}$$

Comparing these with the corresponding expressions in one dimension, Eq. (26), we see that contributions to $\Pi_{\rm mag}$ from the spin degeneracy are independent of the dimensionality. This is simply due to the fact that these contributions are determined only by the occupancy of the spin states at the carrier site. Furthermore, we see that terms due to the intersite coupling assume the same qualitative form in both Eqs. (26) and (29). Only the numerical prefactors of these terms are different. Hence our results for $\Pi_{\rm mag}$ are essentially independent of the dimensionality of the system.

IV. DISCUSSION AND CONCLUSION

We derive the magnetic contribution to the Peltier heat of a small polaron, $\Pi_{\rm mag}$, by calculating the change in entropy upon adding a carrier, at a site of a spin-$\frac{1}{2}$ magnetic semiconductor or insulator. Since the added carrier's exchange interaction is limited to the occupied site and its nearest neighbors, we treat these sites as a cluster. Within each cluster we describe the positive intrasite exchange by the Heisenberg coupling and the intersite exchange by the Ising coupling. The exchange interactions involving sites outside the cluster are treated within the mean-field approximation. At temperatures well below the magnetic transition temperature T_c, $\Pi_{\rm mag}$ is both small and negative. This negative term arises from the local-spin alignment induced by the carrier's exchange interaction with the sites adjacent to it. That is, the augmentation of the intersite exchange arising from the added spin enhances the exchange binding of the cluster, thereby reducing its entropy. This contributes a negative term to the Peltier heat. At temperatures between T_c and that corresponding to the intrasite exchange coupling, $\Pi_{\rm mag}$ is the sum of two comparable terms of opposite sign. The first is the high-temperature manifestation of this carrier-induced spin alignment (spin-polaron) effect, $-\gamma J^2/kT$, where γ

equals $\frac{5}{3}$ and 5 for one- and three-dimensional models, respectively. The second term is the previously proposed[7,8] spin-degeneracy factor $kT\ln(\frac{3}{2})$. Finally, only at the unrealistically high temperatures, $T \gg J_0/k$, does Π_{mag} assume the simple form $kT\ln 2$.

It should be emphasized that both the mean-field approach and the Ising model are inadequate if applied to *all* the spins of the system. In particular, these two simplifications eliminate the two most important contributions to the magnetic portion of the Peltier heat in the paramagnetic regime. Namely, these oversimplifications eliminate the carrier-induced spin alignment and the carrier-induced change of the spin degeneracy, respectively. It is for this reason that we have adopted the cluster models of Secs. II B and III. Comparison of the results of these calculations, Eqs. (26) and (29), with that of a mean-field Ising calculation, Eq. (15), illustrate these points.

Finally, although the calculations presented in this paper are for ferromagnetic systems, we have also carried out similar calculations for a two-sublattice antiferromagnet. The results for Π_{mag} are as in the ferromagnetic case, except that the intersite exchange integral J (defined as positive in the ferromagnetic case) is replaced by its absolute value in the antiferromagnetic case.

Electrical-transport experiments on MnO provide one example of a system to which this work is applicable. In particular, the Peltier heat of a hole small polaron has been measured above the Néel temperature in the Li-doped antiferromagnetic insulator MnO.[10,11] The Peltier heat is found to increase linearly with temperature between 200 and 900 K. As shown in the present work, the magnetic contribution to the Peltier heat does increase with temperature, albeit not as rapidly as these experiments indicate. However, the nonmagnetic contribution to the Peltier heat can also increase with temperature.[11] This is caused by the shift of the Fermi energy with temperature. This shift reflects temperature-dependent changes of the occupation probabilities of various dopants and (unknown) defects of this compensated semiconductor. Clearly, unambiguous observation of the magnetic contribution to the Peltier heat in such a complicated situation is extremely difficult.

Nonetheless, one conclusion of the present work is that the magnetic contribution to the Peltier heat is generally significant. As such, it should be included in an analysis of the Peltier heat of a magnetic semiconductor. Presently this has not been done. Instead, the temperature dependence of the Peltier heat is often totally attributed to temperature-dependent shifts of the chemical potential contained in its nonmagnetic contribution.[11] In effect, we have shown that this is not generally correct. To obtain the shift of the chemical potential with temperature, one must first obtain the nonmagnetic contribution. This requires a subtraction of the magnetic contribution from the total Peltier heat. The present work provides a calculation of the magnetic contribution to the Peltier heat.

In summary, the addition of a carrier to the system produces two competing effects. First, adding the carrier provides an extra degree of freedom (spin up or spin down of the carrier). This tends to increase the entropy of the system, producing a positive contribution to the Peltier heat. Second, however, the added intersite exchange between the occupied site and its neighbors enhances the exchange binding between these sites. This reduces the energetically allowable spin configurations, thereby reducing the entropy of the system. This produces a negative contribution to the Peltier heat. The first effect dominates at high temperatures, and the second effect dominates at low temperatures. Between these two limiting regimes both effects are comparable.

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