

Thermoelectric power of compounds with cerium: Influence of the crystalline field on the Kondo effect

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The influence of the crystalline field on the Kondo effect of compounds with cerium is studied in the framework of an effective Hamiltonian which describes the resonant scattering character of cerium and which takes into account combined spin and orbit exchange scattering. The third-order perturbation-theory thermoelectric power is computed exactly in the case of two levels split by the crystalline field. The model is applied to the thermoelectric-power measurements of $Ce_{1-x}La_xAl_3$ and the agreement with experiment is good, especially for low cerium concentration.

I. INTRODUCTION

Cerium in compounds such as $CeAl_2$ and $CeAl_3$ is magnetic and presents a Kondo effect due to the large resonant scattering which arises from the mixing between conduction and $4f$ electrons, because the cerium $4f$ level is close to the Fermi level. Such cerium compounds exhibit also a crystalline field, which deeply affects the nature of the Kondo effect. The influence of the crystalline field on the Kondo effect in cerium compounds has been extensively studied in the framework of an effective Hamiltonian which takes into account combined spin and orbit exchange scattering.¹ It has been found, in particular, that the magnetic resistivity computed by third-order perturbation behaves logarithmically at low temperatures, then goes generally through a maximum at a temperature corresponding roughly to the over-all crystalline-field splitting and behaves logarithmically at high temperatures, with a slope higher in absolute value than the low-temperature slope. The experimental resistivity of $CeAl_2$ and $CeAl_3$ is accounted for by this model except at very low temperatures; in particular, the resistivity of $CeAl_3$ is still decreasing rapidly with decreasing temperature down to the lowest measured temperature.²

Recent measurements of the thermoelectric power in $Ce_{1-x}La_xAl_3$ compounds³ can provide a new check of the preceding model. The Seebeck coefficients of $Ce_{1-x}La_xAl_3$ present a large positive peak at a temperature between 25 and 50 K and reach "giant" values up to $50 \mu V/K$, as shown in Fig. 6. The thermoelectric power of rare-earth alloys and compounds has been theoretically studied^{4,5} but no precise calculation has been performed in the case of the resonant scattering appropriate to cerium impurities. Peschel and Fulde⁴ have initially considered the case of two

nonmagnetic singlets separated by an energy Δ and they have found a maximum in the Seebeck coefficient at a temperature of order 0.3Δ . Then, Takayama and Fulde⁵ have studied again the thermoelectric power with a general Hamiltonian derived by Hirst,⁶ but no quantitative calculation is available for the resonant scattering. We will compare these previous works to our work in Sec. VI.

The purpose of the present paper is to compute in the perturbation theory the thermoelectric power within the framework of the effective Hamiltonian which describes the resonant scattering and which takes into account both the crystalline field and the combined spin and orbit exchange scattering. Finally, we will apply our theoretical results to the case of $Ce_{1-x}La_xAl_3$ compounds.

II. THEORETICAL MODEL

We will compute the thermoelectric power in the perturbation theory. In presence of a crystalline field (CF), the first perturbation term which yields a nonzero contribution to the thermoelectric power is the third-order term, instead of the fourth-order term in the Kondo problem without CF.⁷ Therefore, we can use the third-order calculations, in particular, the relaxation time, which have been already derived in Ref. 1 for the resistivity and we will take the same notations as in Ref. 1.

Within the framework of the ionic model, the ground-state multiplet of a cerium impurity ($4f^1$ configuration) corresponds to $j = \frac{5}{2}$ ($l = 3$, $s = \frac{1}{2}$). The spin-orbit splitting is known to be much larger than the CF effect, so that we can restrict our consideration to the ground-state multiplet alone. In a CF of hexagonal symmetry, the $j = \frac{5}{2}$ level is split into three doublets, each characterized by a

given j_z^2 value, i. e., $j_z = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}$, respectively correspond to the eigenstates of the three doublets. On the other hand, a CF of cubic symmetry splits the $j = \frac{5}{2}$ level into a doublet Γ_7 and a quartet Γ_8 , the energy eigenstates being linear combinations of the eigenstates of j_z as given in Ref. 1. The following treatment is valid regardless of the symmetry type of the CF. We shall use M to denote the quantum number characterizing a CF eigenstate of energy E_M .

By applying the Schrieffer-Wolff transformation⁸ on the Anderson Hamiltonian, the following Hamiltonian for a Ce impurity in a metallic host has been previously obtained¹:

$$H = \sum_{k, M} \epsilon_k n_{kM} + \sum_M E_M n_M - \sum_{\substack{k, k' \\ M, M'}} J_{MM'} C_{k'}^\dagger C_{kM} C_M^\dagger C_{M'} + \sum_{\substack{k, k' \\ M}} V_{MM} C_{k'}^\dagger C_{kM} C_M \quad (1)$$

Here C_{kM}^\dagger represents the operator for creating a conduction electron of energy ϵ_k in the partial-wave state M (in the subspace of $l=3$, $s=\frac{1}{2}$, and $j=\frac{5}{2}$), while C_M^\dagger represents that for creating an electron in the localized CF state M of the Ce ion. n_{kM} and n_M are the corresponding number operators. The energies ϵ_k and E_M are defined with respect to the Fermi energy. The exchange-coupling parameters are given by

$$J_{MM'} = \frac{1}{2} (|V_{kf}|^2) (1/E_M + 1/E_{M'}), \quad (2)$$

with a cutoff D such that $J_{MM'} = 0$ if $|\epsilon_k|$ or $|\epsilon_{k'}|$ is greater than D ; the cutoff D is chosen to be of order the mean value E_M . V_{kf} denotes the matrix-element of mixing between the $4f$ and the conduction electrons at the Fermi energy. The elements

$$V_{MM} = V_{MM} - J_{MM} \langle n_M \rangle \quad (3)$$

represent pure direct scattering. $\langle n_M \rangle$ is the equilibrium population of the state M . Clearly, for cerium impurities

$$\sum_M \langle n_M \rangle = 1. \quad (4)$$

With the Hamiltonian (1), we follow Kondo's approach⁹ of calculating the scattering amplitude in the second Born approximation. The scattering probability is then calculated up to the third order of perturbation. This calculation has been presented in Ref. 1: here we simply quote the results. The relaxation time of a conduction electron is found to be

$$\tau_k = \frac{(2j+1)\pi\hbar^3}{mkv_0c} \left(\frac{1}{R_k} - \frac{S_k}{R_k^2} \right), \quad (5)$$

where m is the mass of the electron, k is its wave number, v_0 is the sample volume, and c the con-

centration of Ce atoms. R_k and S_k , respectively, denote the second- and third-order term.

At this point, as in Ref. 1 we switch over to indices representing the CF energy levels rather than the eigenstates: let i ($= 1, 2, 3, \dots$) denote the energy level E_i of degeneracy α_i . Then

$$R_k = A + \sum_{i,j}' \frac{d_{ij}}{f_k - p_{ij}}, \quad (6)$$

where the prime on the summation is to indicate that the term $i=j$ is to be omitted. f_k is the Fermi function

$$f_k = (1 + e^{\beta\epsilon_k})^{-1}, \quad (7)$$

$$A = \sum_i \alpha_i \left[V_{ii}^2 + \alpha_i J_{ii}^2 \langle n_i \rangle \left(1 - \frac{\langle n_i \rangle}{\alpha_i} \right) \right], \quad (8)$$

$$p_{ij} = (1 - e^{\beta\Delta_{ij}})^{-1}, \quad (9)$$

with

$$\Delta_{ij} = E_i - E_j \quad (10)$$

and

$$d_{ij} = -p_{ij} \alpha_i \alpha_j J_{ij}^2 \langle n_j \rangle, \quad (11)$$

we have

$$\langle n_i \rangle = e^{-\beta E_i} / \sum_i \alpha_i e^{-\beta E_i}. \quad (12)$$

In Eq. (6) the first term represents elastic scattering, while the sum gives inelastic processes.

The third-order term can be written

$$S_k = \sum_{i,l} C_i^l g(\epsilon_k + \Delta_{li}) + \sum_{\substack{i,j,l \\ (i \neq j)}} D_{ij}^l \frac{g(\epsilon_k + \Delta_{li})}{f_k - p_{ij}}, \quad (13)$$

where

$$g(\omega) = \sum_q \frac{f_q - \frac{1}{2}}{\epsilon_q - \omega} \approx \sum_q \frac{f_q}{\epsilon_q - \omega} \quad (14)$$

is the usual function appearing in the Kondo problem and

$$C_i^l = 2\alpha_i [J_{ii} J_{il}^2 \langle n_i \rangle (\alpha_i \alpha_l - \delta_{il}) - V_{ii} J_{ii}^2 \alpha_l (\langle n_i \rangle - \langle n_l \rangle)], \quad (15)$$

$$D_{ij}^l = -2p_{ij} J_{ij} J_{il} J_{ji} \alpha_i \alpha_j \alpha_l \langle n_j \rangle. \quad (16)$$

Clearly, we have

$$d_{ji} = -d_{ij}, \quad D_{ij}^l = -D_{ji}^l. \quad (17)$$

Note that in writing Eq. (13) for S_k , terms of third order that are not proportional to the function $g(\omega)$ have been neglected.

III. DERIVATION OF THERMOELECTRIC POWER

The thermoelectric power is given by the classical formula

$$S = -\frac{1}{eT} \left[\int_{-\infty}^{\infty} \epsilon_k \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) \tau_k d\epsilon_k / \int_{-\infty}^{\infty} \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) \tau_k d\epsilon_k \right], \quad (18)$$

with $e > 0$.

It is easy to check that R_k given by Eq. (6) is an even function of ϵ_k so that

$$\int_{-\infty}^{\infty} \epsilon_k \left(\frac{1}{R_k} \right) \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) d\epsilon_k = 0. \quad (19)$$

Thus,

$$S = \frac{1}{eT} \frac{1}{\sigma^{(2)}} \int_{-\infty}^{\infty} \frac{S_k}{R_k^2} \epsilon_k \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) d\epsilon_k, \quad (20)$$

where

$$\sigma^{(2)} = \int_{-\infty}^{\infty} \frac{1}{R_k} \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) d\epsilon_k. \quad (21)$$

The inversion of R_k has been worked out in Ref. 1,

$$\frac{1}{R_k} = \frac{1}{A} \left(1 - \sum_{i,j} \frac{\mu_{ij}}{f_k - \lambda_{ij}} \right), \quad (22)$$

where λ_{ij} are the roots of $R_k(f_k) = 0$. We follow the method of Ref. 1: the labeling scheme is such that for negative p_{ij} values, λ_{ij} is the root closest to and smaller than p_{ij} , whereas for positive p_{ij} values, λ_{ij} is the root closest to and greater than p_{ij} . The coefficients μ_{ij} have been explicitly given in Ref. 1. It can be shown that

$$\lambda_{ij} + \lambda_{ji} = 1, \quad \mu_{ij} = -\mu_{ji}. \quad (23)$$

It turns out to be convenient to write (in analogy to p_{ij})

$$\lambda_{ij} = (1 - e^{\beta \Delta_{ij}^0})^{-1}, \quad (24)$$

i. e.,

$$\Delta_{ij}^0 = (1/\beta) \ln(1 - 1/\lambda_{ij}). \quad (25)$$

Then, we have

$$\Delta_{ij}^0 = -\Delta_{ji}^0. \quad (26)$$

One easily obtains

$$\sigma^{(2)} = \frac{1}{A} \left(1 - \sum_{i,j} \mu_{ij} \beta \Delta_{ij}^0 \right). \quad (27)$$

Now, we have

$$\frac{1}{R_k^2} = \frac{1}{A^2} \left(1 + \sum_{i,j} \frac{\mu_{ij}^2}{(f_k - \lambda_{ij})^2} - 2 \sum_{i,j} \frac{\mu_{ij} \gamma_{ij}}{f_k - \lambda_{ij}} \right), \quad (28)$$

where

$$\gamma_{ij} = 1 - \sum_{m,n} \frac{\mu_{mn}}{\lambda_{ij} - \lambda_{mn}}. \quad (29)$$

The symbol $\sum'_{m,n}$ means that we sum over m and n except for $m=n$ and $mn=ij$. Clearly, we have

$$\gamma_{ij} = \gamma_{ji}. \quad (30)$$

We thus obtain S_k/R_k^2 by multiplying Eq. (13) by (28). By defining

$$G_n(\delta, \delta') \equiv \frac{1}{n(\epsilon_F)} \int_{-\infty}^{\infty} \beta \epsilon_k \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) \times \frac{g(\epsilon_k + \delta)}{[1 - f_k(1 - e^{\beta \delta'})]^n} d\epsilon_k, \quad (31)$$

we finally obtain

$$S = \frac{k_B}{e} \frac{1}{\sigma^{(2)}} \frac{n(\epsilon_F)}{A^2} \left(\sum_{i,l} C_i^l G_1(\Delta_{li}, 0) + \sum_{n,n'} \sum_{i,l} [U_{nn'}^{il} G_1(\Delta_{li}, \Delta_{nn'}^0) + V_{nn'}^{il} G_2(\Delta_{li}, \Delta_{nn'}^0)] \right), \quad (32)$$

where $n(\epsilon_F)$ is the density of states at the Fermi level for one spin direction, and

$$U_{nn'}^{il} = \frac{1}{\lambda_{nn'}} \left[2\mu_{nn'} \gamma_{nn'} C_i^l + \sum_{j(\neq i)} D_{ij}^l \left(\frac{\mu_{nn'}^2}{(\lambda_{nn'} - p_{ij})^2} + \frac{2\mu_{nn'} \gamma_{nn'}}{\lambda_{nn'} - p_{ij}} \right) \right], \quad (33)$$

$$V_{nn'}^{il} = \left(\frac{\mu_{nn'}}{\lambda_{nn'}} \right)^2 \left(C_i^l + \sum_{j(\neq i)} \frac{D_{ij}^l}{\lambda_{nn'} - p_{ij}} \right). \quad (34)$$

The calculation can be considerably simplified by using some symmetry properties of the intergrals $G_n(\delta, \delta')$. Let us introduce:

$$\Gamma_n(\delta, \delta') \equiv \frac{1}{n(\epsilon_F)} \int_{-\infty}^{\infty} \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) \times \frac{g(\epsilon_k + \delta)}{[1 - f_k(1 - e^{\beta \delta'})]^n} d\epsilon_k. \quad (35)$$

By noting that $g(\omega) = g(-\omega)$, and also that for $\epsilon_k = \epsilon_k + \delta$,

$$-\frac{\partial f_k}{\partial \epsilon_k} = \frac{e^{\beta \delta}}{[1 - f_k(1 - e^{\beta \delta})]^2} \left(-\frac{\partial f_k}{\partial \epsilon_k} \right),$$

it is easy to deduce the following relations:

$$G_2(\delta, \delta') = e^{-\beta \delta'} [G_1(\delta + \delta', 0) + \beta \delta' \Gamma_1(\delta + \delta', 0)], \quad (36a)$$

$$G_1(\delta, \delta') = \frac{e^{\beta(\delta + \delta')} - 1}{e^{\beta \delta'} - 1} [G_1(0, \delta + \delta') - \beta \delta \Gamma_1(0, \delta + \delta')] + \frac{1 - e^{\beta \delta}}{e^{\beta \delta'} - 1} [G_1(0, \delta) - \beta \delta \Gamma_1(0, \delta)], \quad (36b)$$

$$G_1(-\delta, \delta') = -e^{-\beta \delta'} G_1(\delta, -\delta'), \quad (36c)$$

$$\Gamma_1(-\delta, \delta') = e^{-\beta \delta'} \Gamma_1(\delta, -\delta'). \quad (36d)$$

In order to calculate S we thus need to evaluate only four integrals: $G_1(\delta, 0)$, $G_1(0, \delta)$, $\Gamma_1(\delta, 0)$, $\Gamma_1(0, \delta)$. This is done in Appendix A, by using the expression of $g(\omega)$ in terms of the digamma func-

tion¹⁰

$$g(\omega) = n(\epsilon_F) \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\omega}{2\pi T} \right) \right], \quad (37)$$

where D and ω are expressed in K. The results are (with δ expressed in K)

$$\Gamma_1(0, \delta) = \frac{\delta/T}{e^{\delta/T} - 1} \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(i \frac{\delta}{2\pi T} \right) - 1 \right], \quad (38a)$$

$$\Gamma_1(\delta, 0) = \ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(i \frac{\delta}{2\pi T} \right) - 1 - \frac{\delta}{2\pi T} \operatorname{Im} \psi' \left(i \frac{\delta}{2\pi T} \right), \quad (38b)$$

$$G_1(0, \delta) = \frac{(\delta/T)^2}{2(e^{\delta/T} - 1)} \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(i \frac{\delta}{2\pi T} \right) - \frac{1}{2} \right], \quad (38c)$$

$$G_1(\delta, 0) = \frac{\delta}{2T} \left[1 + \frac{\delta}{2\pi T} \operatorname{Im} \psi' \left(i \frac{\delta}{2\pi T} \right) \right]. \quad (38d)$$

Here $\psi(z)$ and $\psi'(z)$ are the digamma and trigamma functions, respectively.

Equation (32), in conjunction with Eqs. (36a) and (36b) and (38a)–(38d), provides a closed-form expression for the CF-induced Seebeck coefficient obtained in the third-order perturbation calculation. As is well known, in the absence of CF splitting, i. e., if $\Delta_{ij} = 0$ the third-order calculation yields a zero thermoelectric power and the first nonzero perturbation order is the fourth one.

IV. CASE OF TWO LEVELS SPLIT BY THE CRYSTALLINE-FIELD EFFECT

Up to this point, our treatment is completely general with respect to the number of levels split by the CF effect. In this section, we present the results for the Seebeck coefficient in the particular case of two levels split by the CF for a cerium impurity ($\alpha_1 + \alpha_2 = 6$).

The calculation of the Seebeck coefficient proceeds from the general formula (32), but, in the two level case, the roots λ_{ij} and the coefficients μ_{ij} can be expressed analytically. So, it results that the thermoelectric power can be written analytically in the case of two levels. The derivation, although straightforward, is rather tedious; the final expression is given in Appendix B.

We have summarized in Figs. 1–3 the main results concerning the Seebeck coefficient in the two level case. The mixing parameter V_{kf} used in (2) is taken equal to $V_{kf} = 0.07$ eV throughout the paper; similarly the density of states $n(\epsilon_F)$ involved in (32) is also taken constant and equal to $n(\epsilon_F) = 2.2$ states/eV atom which is the density of states of pure lanthanum.¹¹ Thus, there are five remaining parameters: the cutoff D , the ground-state degeneracy α_1 , the direct scattering potential \mathfrak{U} which is assumed to be independent of the con-

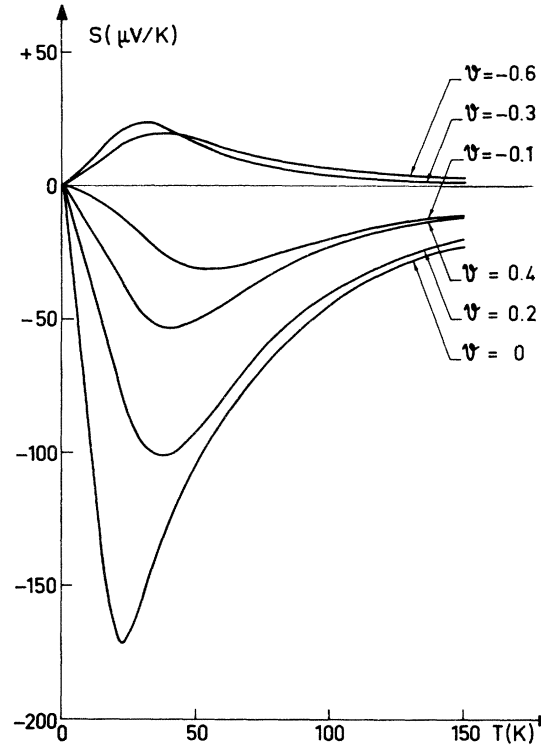


FIG. 1. Seebeck coefficient S (expressed in $\mu\text{V/K}$) vs temperature T (in K) in the exact two-level case: dependence on \mathfrak{U} (in eV). The parameters used here are: $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, $\alpha_1 = 2$, $\alpha_2 = 4$, $\Delta = 150$ K, $J_{11} = -0.15$ eV.

sidered level, the exchange integral J_{11} , and the CF splitting $\Delta = \Delta_{21}$.

We have found that the Seebeck coefficient is quite insensitive to the considered value for the cutoff D . So, we have chosen D equal to $D = 850$ K which is the value adopted for the resistivity of CeAl_3 in Ref. 1 and we keep D equal to that value in the following.

On the other hand, the dependence of the thermoelectric power on Δ is significant, but not really drastic if we restrict ourselves to values of Δ typical for cerium impurities. So, we choose here $\Delta = 150$ K and we keep this value constant in Figs. 1–3.

Therefore, the parameters that we make vary in Figs. 1–3 are essentially \mathfrak{U} , J_{11} , and α_1 . Figure 1 gives the variation of the thermoelectric power with \mathfrak{U} for a doublet ground state; the different parameters are $\Delta = 150$ K, $\alpha_1 = 2$, $\alpha_2 = 4$, $J_{11} = -0.15$ eV, and \mathfrak{U} is ranging from -0.6 to 0.4 eV. We see that a “giant” negative thermoelectric power is obtained for $\mathfrak{U} = 0$, in contrast to the results of Takayama and Fulde⁵; this point is discussed later. The addition of the direct scattering potential \mathfrak{U} makes the thermoelectric power S

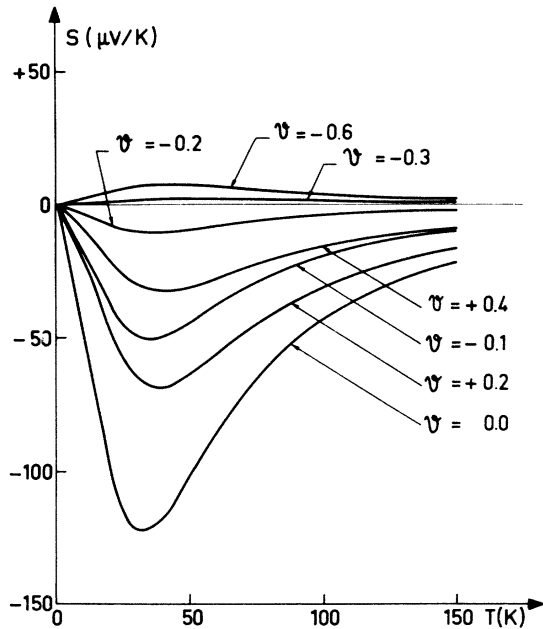


FIG. 2. Seebeck coefficient S (expressed in $\mu\text{V}/\text{K}$) vs temperature T (in K) in the exact two-level case: dependence on ν (in eV). The parameters used here are: $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, $\alpha_1 = 4$, $\alpha_2 = 2$, $\Delta = 150$ K, $J_{11} = -0.15$ eV.

increase; in particular S becomes positive for relatively large negative values of ν . In the example of Fig. 1, with $\Delta = 150$ K, the temperature of the peak varies with ν from 23 to 55 K. Therefore, the peak of the Seebeck coefficient S occurs at a fraction of Δ , ranging between roughly $\Delta/6$ and $\Delta/3$, while the maximum of the resistivity occurs roughly at Δ .

Figure 2 gives the variation of the thermoelectric power with ν for a quartet ground state; the different parameters are $\Delta = 150$ K, $\alpha_1 = 4$, $\alpha_2 = 2$, $J_{11} = -0.15$ eV, and ν is ranging from -0.6 to 0.4 eV. A "giant" thermoelectric power is also obtained for $\nu = 0$ and the thermoelectric power increases with the absolute values of ν . A large positive S value can be obtained for negative and relatively large J_{11} and ν values; for instance, with $\Delta = 130$ K, $J_{11} = -0.3$ eV, and $\nu = -0.8$ eV give a peak of $22 \mu\text{V}/\text{K}$ at 26 K. Therefore, we obtain for $\alpha_1 = 4$ the same S values as for $\alpha_1 = 2$, but with $|J_{11}|$ and $|\nu|$ much larger than generally used for cerium impurities.¹

Finally, Fig. 3 gives the variation of the thermoelectric power S with J_{11} for a doublet ground state ($\alpha_1 = 2$, $\alpha_2 = 4$) and for two values of ν : $\nu = 0$ and $\nu = -0.3$ eV. In the case of $\nu = 0$, S is negative and its absolute value increases regularly with increasing $|J_{11}|$ values: the different curves are roughly homothetic with a peak occurring at roughly the same temperature of $\Delta/6$. On the contrary,

in the case of $\nu = -0.3$ eV, the shape of the curves does not remain constant: S increases at low temperatures with $|J_{11}|$ and decreases at high temperatures; moreover, S changes sign when J_{11} and ν become roughly comparable, for instance in the case $\nu = -0.3$ eV and $J_{11} = -0.2$ eV; we can also note that, in the case $\nu = -0.3$ eV, the temperature of the maximum decreases with an increasing $|J_{11}|$ value.

Thus, in the two-level case, we obtain giant thermoelectric power values the sign and the magnitude of which vary with essentially ν and α_1 but also with J_{11} and Δ .

V. " $f_k = \frac{1}{2}$ APPROXIMATION" AND THE CASE OF THREE LEVELS

Equation (32) represents an exact expression for the third-order-perturbation calculation of S . As seen in Sec. IV, the calculation can be carried out analytically in the two-level case, but according to Appendix B the calculation is rather tedious. On the other hand, in the case of three or more than three CF levels, the roots λ_{ij} and the coefficients μ_{ij} have to be determined numerically and finally the calculation becomes rapidly inextricate.

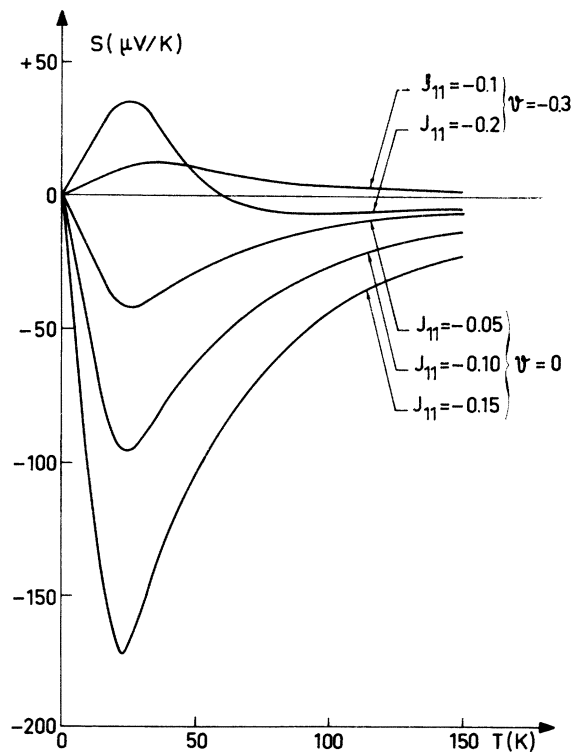


FIG. 3. Seebeck coefficient S (expressed in $\mu\text{V}/\text{K}$) vs temperature T (in K) in the exact two-level case: dependence on J_{11} (in eV) for two values of ν : $\nu = 0$ and $\nu = -0.3$ eV. The other parameters used here are: $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, $\alpha_1 = 2$, $\alpha_2 = 4$, $\Delta = 150$ K.

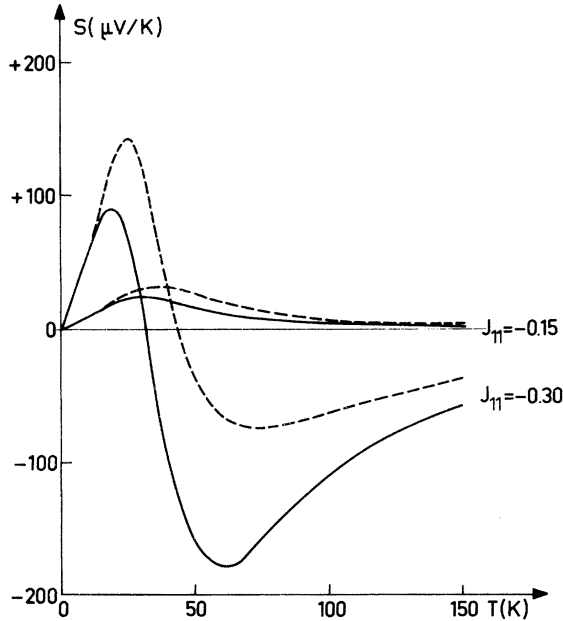


FIG. 4. Seebeck coefficient S (expressed in $\mu\text{V}/\text{K}$) vs temperature T (in K) in the two-level case: comparison between the exact calculation (full lines) and the " $f_k = \frac{1}{2}$ approximation" (dashed lines) for two values of J_{11} : $J_{11} = -0.15$ eV and $J_{11} = -0.3$ eV. The other parameters used here are: $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, $\alpha_1 = 2$, $\alpha_2 = 4$, $\Delta = 150$ K, $v = -0.3$ eV.

Thus, in order to have an idea of the variation of the thermoelectric power in the case of more than two levels, we can use the so-called " $f_k = \frac{1}{2}$ approximation," which consists in replacing f_k in the denominators of R_k and S_k by its Fermi level value $\frac{1}{2}$.¹ In this section we will first compare the exact result and the $f_k = \frac{1}{2}$ approximation result in the case of two levels and then we will briefly describe the case of three levels.

The $f_k = \frac{1}{2}$ approximation yields an energy-independent R_k term that we call R ,

$$R = R_k = A + \sum_{ij} \frac{d_{ij}}{\frac{1}{2} - p_{ij}}, \quad (39)$$

so that the thermoelectric power is given by

$$S = \frac{k_B}{e} \frac{1}{R} \int_{-\infty}^{+\infty} \left(-\frac{\partial f_k}{\partial \epsilon_k} \right) \beta \epsilon_k S_k d\epsilon_k, \quad (40)$$

where S_k is equal to

$$S_k = \sum_{i,l} C_{il}^i g(\epsilon_k + \Delta_{li}) + \sum_{\substack{i,j,l \\ (i \neq j)}} D_{ij}^i \frac{g(\epsilon_k + \Delta_{li})}{\frac{1}{2} - p_{ij}}. \quad (41)$$

By use of the definition (31), S becomes

$$S = \frac{k_B}{e} \frac{n(\epsilon_F)}{R} \sum_{i,l} \gamma_i^l G_1(\Delta_{li}, 0), \quad (42)$$

where

$$\gamma_i^l = C_{il}^i + \sum_{j(i \neq l)} \frac{D_{ij}^i}{\frac{1}{2} - p_{ij}}. \quad (43)$$

If we use the symmetry relation (36c) for $G_1(\delta, 0)$, the expression (42) can be also written again as

$$S = \frac{k_B}{e} \frac{n(\epsilon_F)}{R} \sum_{\substack{i,l \\ (i < l)}} (\gamma_i^l - \gamma_l^i) G_1(\Delta_{li}, 0). \quad (44)$$

The comparison between the $f_k = \frac{1}{2}$ approximation results and the exact ones computed numerically from the expression (32) is shown in Fig. 4 in the two-level case. The parameters used in Fig. 4 are $\Delta = 150$ K, $\alpha_1 = 2$, $\alpha_2 = 4$, $v = -0.3$ eV, and two values of J_{11} , i. e., $J_{11} = -0.15$ and -0.3 eV. We have chosen these two cases because they represent two typical cases for the behavior of S . We see that the $f_k = \frac{1}{2}$ approximation result differs noticeably from the exact one by an amount which can reach 50% of the exact value; from that point of view, the thermoelectric power differs from the resistivity where the difference between the $f_k = \frac{1}{2}$ approximation calculation and the exact one is much smaller. However, as shown on Fig. 4, in spite of the differences in magnitude, the shapes of the thermoelectric power curves and their qualitative features are the same. Therefore, we believe the same would be true for the case of three levels or even more than three levels.

Figure 5 shows the thermal variation of the Seebeck coefficient computed in the $f_k = \frac{1}{2}$ approxima-

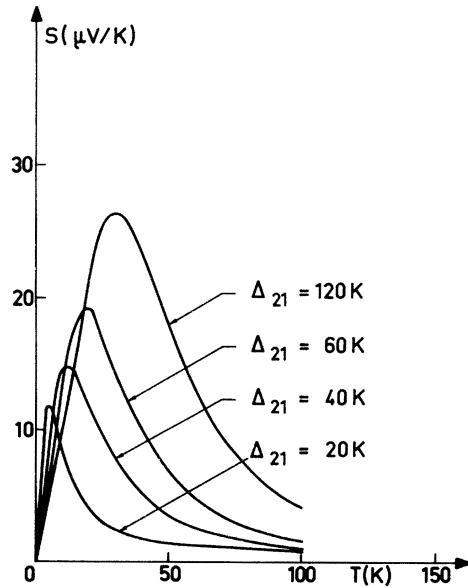


FIG. 5. Seebeck coefficient S (expressed in $\mu\text{V}/\text{K}$) vs temperature T (in K) in the three-level case treated in the " $f_k = \frac{1}{2}$ approximation": dependence on Δ_{21} (in K). The parameters used here are: $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, $\alpha_1 = \alpha_2 = \alpha_3 = 2$, $\Delta_{31} = 130$ K, $J_{11} = -0.145$ eV, $v = -0.28$ eV.

tion for the case of three levels split by the CF effect. The parameters used in Fig. 5 are $D = 850$ K, $n(\epsilon_F) = 2.2$ states/(eV atom), $\nu = -0.28$ eV, $J_{11} = -0.145$ eV, $\alpha_1 = \alpha_2 = \alpha_3 = 2$, an over-all CF splitting $\Delta_{31} = 130$ K and a distance Δ_{21} between the ground state and the first excited state varying between 20 and 120 K. We have chosen here the parameters which will be used in Fig. 6 for $\text{Ce}_{0.01}\text{La}_{0.99}\text{Al}_3$, except that we will take the two-level case with a doublet ground state. Therefore, Fig. 5 is useful to compare the three-level case to the two level with a doublet ground state, when the over-all splitting is the same in the two cases. We observe in Fig. 5 that, when Δ_{21} increases we obtain both an increase of the magnitude of the peak and an increase of the temperature of the peak which occurs at roughly $\Delta_{21}/3$. Even for a Δ_{21} value much smaller than Δ_{31} , there is only one peak which becomes broader when Δ_{21} increases. Finally, all the curves with Δ_{21} varying from 20 to 120 K have essentially the same shape, with only a change in the location and the magnitude of the peak.

VI. COMPARISON WITH EXPERIMENTS AND CONCLUDING REMARKS

In previous papers, we have applied our model to the resistivity of CeAl_2 and CeAl_3 compounds at normal pressure⁴ or under high pressure^{12,13} and reasonable fits have been obtained except at very low temperatures. Here we would like to finally apply our model to the giant Seebeck coefficients of $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ compounds. Figure 6 shows the experimental values of the "magnetic" Seebeck coefficient of $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ for $x = 0.99$, 0.9, 0.5, and 0, as well as the four corresponding theoretical curves. The experimental "magnetic" Seebeck coefficient corresponds to the difference between the measured Seebeck coefficients of $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ and of LaAl_3 (Ref. 3); this procedure which is equivalent to the Matthiessen rule is certainly justified here because the magnetic Seebeck coefficient and the corresponding value for LaAl_3 are never of the same order of magnitude. The $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ have a hexagonal crystallographic structure so that the $j = \frac{5}{2}$ multiplet of cerium is split into three doublets. However, since we cannot really evaluate both the distances Δ_{21} and Δ_{31} only by resistivity or thermoelectric power experiments and since moreover the Seebeck coefficient keeps the same shape in the three-level case as in the two-level case with a doublet ground state according to Fig. 5, we have determined the theoretical curves of Fig. 6 by taking the exact two-level case with $\alpha_1 = 2$ and $\alpha_2 = 4$; we have taken also $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K and only Δ , ν , and J_{11} are considered as adjustable parameters. The value of the maximum

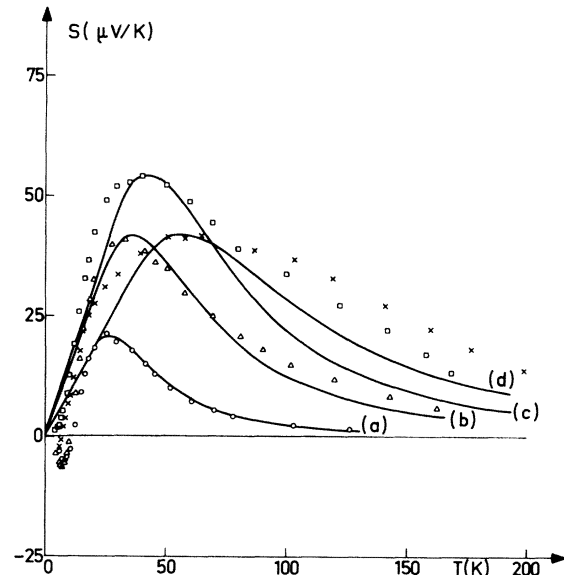


FIG. 6. Comparison between experiment and theory for $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$. Experimental points show the differences between the Seebeck coefficients of $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ and of LaAl_3 for $x = 0.99$ (○), 0.90 (△), 0.50 (□), 0 (×). The theoretical curves correspond to the exact two level case ($\alpha_1 = 2$, $\alpha_2 = 4$) for $V_{kf} = 0.07$ eV, $n(\epsilon_F) = 2.2$ states/eV atom, $D = 850$ K, and the following set of parameters: curve (a): $\Delta = 130$ K, $\nu = -0.27$ eV, $J_{11} = -0.145$ eV (i. e., $E_1 = -395$ K); curve (b): $\Delta = 166$ K, $\nu = -0.7$ eV, $J_{11} = -0.2$ eV (i. e., $E_1 = -285$ K); curve (c): $\Delta = 203$ K, $\nu = -0.85$ eV, $J_{11} = -0.195$ eV (i. e., $E_1 = -290$ K); curve (d): $\Delta = 255$ K, $\nu = -0.93$ eV, $J_{11} = -0.16$ eV (i. e., $E_1 = -355$ K).

temperature yields an estimation of Δ and the shape of the curve allows to determine also ν and J_{11} . Curve (a) (obtained with $\Delta = 130$ K, $\nu = -0.27$ eV, $J_{11} = -0.145$ eV) gives an excellent fit of the $\text{Ce}_{0.01}\text{La}_{0.99}\text{Al}_3$ curve from 10 to 130 K; curve (b) ($\Delta = 166$ K, $\nu = -0.7$ eV, $J_{11} = -0.2$ eV) provides a good fit for $\text{Ce}_{0.1}\text{La}_{0.9}\text{Al}_3$, while curves (c) ($\Delta = 203$ K, $\nu = -0.85$ eV, $J_{11} = -0.195$ eV) and (d) ($\Delta = 255$ K, $\nu = -0.93$ eV, $J_{11} = -0.16$ eV) yield worse fits to the two cerium-concentrated compounds, although both the location and the magnitude of the maxima are well described by these choices of parameters. Therefore, while the exchange integral J_{11} remains roughly constant leading to a value of E_1 between 300 and 400 K, the two other parameters Δ and ν are found to increase rapidly with cerium concentration. Indeed, the values for the different parameters [except those used for the curves (a)] cannot be considered too seriously because of both our approximations and the absence of a very good fit. However, two positive conclusions can be drawn from the analysis of Fig. 6: First, the fit (a) of the 1% cerium compound, which is the only one to be really justified in our one impurity model, is excellent and the deduced

parameters are quite realistic for a cerium impurity; in particular, the values of J_{11} and $|\mathcal{U}|$ agree with the values deduced by the analysis of the resistivity of CeAl_3 and the difference of sign for \mathcal{U} has no real meaning because only the thermoelectric power experiments can determine the sign of \mathcal{U} . Second, the over-all splitting Δ increases with cerium concentration, exactly as for the resistivity of CeAl_3 under applied pressure¹³; the increase of Δ both with Ce concentration and applied pressure can be well understood because the lattice parameters decrease in the two cases.

The crystalline-field over-all splitting of CeAl_3 has been found to be 50 K from fitting resistivity experiments,¹ 255 K here from thermoelectric power ones, 113.6 K from specific-heat measurements,¹⁴ and 280 K from magnetic susceptibility data.¹⁵ The large variation of S with the cerium concentration, the relatively bad fits shown by curves (c) and (d) and the too large values of \mathcal{U} obtained for the cerium-concentrated compounds seem together to indicate that our one-impurity model is perhaps not very good for large cerium concentrations. In particular, the interactions between magnetic impurities, which have been seen to increase the thermoelectric power,¹⁶ could eventually explain the variation of S with cerium concentration.

We can also observe that the theoretical curves of Fig. 6 cannot fit the experimental data at very low temperatures, i. e., below 10 K. In this region, S can become negative and changes with the cerium concentration. Similarly, the resistivity of CeAl_3 is still decreasing with decreasing temperature down to² 0.3 K; magnetic susceptibility,² magnetization,¹⁷ and specific-heat¹⁴ measurements on CeAl_3 suggest also that a transition into a non-magnetic state occurs at low temperatures. We can think that the disappearance of the magnetic moment at low temperatures is due to the Kondo effect and the Kondo temperature of CeAl_3 has been estimated to be 5 K according to Edelstein *et al.*¹⁷; moreover, the Kondo effect of CeAl_3 is certainly peculiar because cerium atoms lie on an ordered lattice and the decrease of the resistivity with decreasing temperature must be connected to that effect.

Giant thermoelectric powers have been also observed in other cerium compounds such as CeSn_3 , CeBe_{13} , or CePb_3 ,¹⁸ but the large maxima encountered in these compounds are also probably connected to a gradual change of valence when temperature decreases. Anomalies in the thermopower have been also observed in the dilute LaCe ,¹⁹ or YCe ,²⁰ alloys. A small negative minimum is observed in LaCe at around 20 K and it is independent of the nominal cerium concentration.¹⁹ Since the Kondo temperature of LaCe is of order 0.1 K,²¹

the presence of a minimum at 20 K, if it is really due to cerium impurities,¹⁹ indicates probably that the first CF excited level lies 60 to 100 K above the ground state. A small positive peak is also observed in YCe at around 20 K (Ref. 20); since the Kondo temperature of YCe is close to 20 K, we can attribute the peak of the thermopower to the Kondo effect itself.

The theoretical results that we have derived here differ from those of Fulde and co-workers,^{4,5} because we start from the effective Hamiltonian which describes the resonant scattering and takes into account combined spin and orbit exchange scattering. In particular, Takayama and Fulde⁵ have found that the isotropic exchange interaction by itself is practically excluded from being the origin of a giant thermopower; on the contrary, we obtain here a giant contribution when only the resonant exchange mechanism is taken into account, i. e., when $\mathcal{U} = 0$. This point indicates that the Hamiltonian (1) is well appropriate to describe the giant Seebeck coefficient of Cerium compounds, as it was already recognized for the resistivity. Moreover, our calculation is performed for any value of the ratio \mathcal{U}/J and not in the usual limit $|\mathcal{U}| \gg |J|$. It results that there is a large Seebeck coefficient S even when $\mathcal{U} = 0$ and that also the sign of S is not only function of the ratio \mathcal{U}/J , as it was the case for Peschel and Fulde.⁴

Thus, the present model which describes both the Kondo and the crystalline field effects yields giant thermoelectric powers which have a peak at a temperature between $\Delta/6$ and $\Delta/3$. In particular, a giant negative Seebeck coefficient is found when only the resonant exchange scattering mechanism is considered, but large positive values result in the presence of an attractive direct potential, which accounts for the giant thermoelectric power of $\text{Ce}_{1-x}\text{La}_x\text{Al}_3$ compounds.

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APPENDIX A

We wish here to evaluate the four integrals: $\Gamma_1(0, \delta)$, $\Gamma_1(\delta, 0)$, $G_1(0, \delta)$, and $G_1(\delta, 0)$. We start from the definition

$$\Gamma_1(\delta, \delta') = \frac{1}{n(\epsilon_F)} \int_{-\infty}^{\infty} \frac{-\partial f_k / \partial \epsilon_k}{1 - f_k(1 - e^{\beta\delta'})} g(\epsilon_k + \delta) d\epsilon_k, \quad (\text{A1})$$

$$G_1(\delta, \delta') = \frac{1}{n(\epsilon_F)} \int_{-\infty}^{\infty} \frac{(-\partial f_k / \partial \epsilon_k) \beta \epsilon_k}{1 - f_k(1 - e^{\beta\delta'})} g(\epsilon_k + \delta) d\epsilon_k. \quad (\text{A2})$$

Now, we have

$$\frac{-\partial f_k / \partial \epsilon_k}{1 - f_k(1 - e^{\beta\delta'})} = \frac{\beta}{(1 + e^{-\beta\epsilon_k})(e^{\beta\epsilon_k} + e^{\beta\delta'})} \quad (\text{A3})$$

and¹⁰

$$g(\epsilon_k + \delta) = n(\epsilon_F) \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\epsilon_k + \delta}{2\pi T} \right) \right], \quad (\text{A4})$$

with δ expressed in K. Thus, we have

$$\Gamma_1(\delta, \delta') = \int_{-\infty}^{\infty} \frac{dx}{(1+e^{-x})(e^x + e^{\delta'/T})} \times \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} + i \frac{x}{2\pi} \right) \right], \quad (\text{A5})$$

$$G_1(\delta, \delta') = \int_{-\infty}^{\infty} \frac{x dx}{(1+e^{-x})(e^x + e^{\delta'/T})} \times \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} + i \frac{x}{2\pi} \right) \right]. \quad (\text{A6})$$

Let us define

$$g(\alpha) \equiv \int_{-\infty}^{\infty} dx \frac{e^{\alpha x}}{(1+e^{-x})(e^x + e^{\delta'/T})}. \quad (\text{A7})$$

For $-1 < \operatorname{Re} \alpha < +1$, $g(\alpha)$ can be evaluated by using the integral (3.223.1) of Gradshteyn *et al.*,²²

$$g(\alpha) = \frac{\pi}{e^{\delta'/T} - 1} \frac{e^{\alpha \delta'/T} - 1}{\sin \alpha \pi}, \quad -1 < \operatorname{Re} \alpha < +1. \quad (\text{A8})$$

Then, we have

$$I_n(\delta') \equiv \int_{-\infty}^{\infty} \frac{x^n dx}{(1+e^{-x})(e^x + e^{\delta'/T})} = \frac{d^n}{d\alpha^n} g(\alpha) \Big|_{\alpha=0}. \quad (\text{A9})$$

Clearly, we have

$$I_0(\delta') = \frac{\delta'/T}{e^{\delta'/T} - 1} \quad (\text{A10})$$

and

$$I_1(\delta') = \frac{(\delta'/T)^2}{2(e^{\delta'/T} - 1)}. \quad (\text{A11})$$

Thus, we can write

$$\Gamma_1(\delta, \delta') = \left[\ln \left(\frac{2\pi T}{D} \right) + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} \right) \right] \times I_0(\delta') + g_0(\delta, \delta'), \quad (\text{A12})$$

$$G_1(\delta, \delta') = \left[\ln \frac{2\pi T}{D} + \operatorname{Re} \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} \right) \right] \times I_1(\delta') + g_1(\delta, \delta'), \quad (\text{A13})$$

where

$$g_n(\delta, \delta') \equiv \int_{-\infty}^{\infty} \frac{x^n dx}{(1+e^{-x})(e^x + e^{\delta'/T})} \times \operatorname{Re} \left[\psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} + i \frac{x}{2\pi} \right) - \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} \right) \right]. \quad (\text{A14})$$

In order to calculate $g_n(\delta, \delta')$ we shall make use of

Gauss's integral formula²³ for $\psi(z)$,

$$\psi(z) = \int_0^{\infty} \left(\frac{e^{-t}}{t} - \frac{e^{-tz}}{1-e^{-t}} \right) dt, \quad \operatorname{Re} z > 0. \quad (\text{A15})$$

Then, we have

$$\psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} + i \frac{x}{2\pi} \right) - \psi \left(\frac{1}{2} + i \frac{\delta}{2\pi T} \right) = \int_0^{\infty} \frac{e^{-(1/2 + i\delta/2\pi T)t}}{1-e^{-t}} (1 - e^{-(i/2\pi)x t}) dt. \quad (\text{A16})$$

Thus, we obtain

$$g_n(\delta, \delta') = \operatorname{Re} \int_0^{\infty} dt \frac{e^{-(1/2 + i\delta/2\pi T)t}}{1-e^{-t}} \times \left(I_n(\delta') - \frac{d^n}{d\alpha^n} g(\alpha) \Big|_{\alpha=-it/2\pi} \right), \quad (\text{A17})$$

that is

$$g_0(\delta, \delta') = \frac{\delta'/T}{e^{\delta'/T} - 1} \operatorname{Re} \int_0^{\infty} \frac{e^{-i(\delta/2\pi T)t}}{2 \sinh(\frac{1}{2}t)} \times \left(1 - i \frac{\pi}{\sinh(\frac{1}{2}t)} \frac{e^{-i(\delta'/2\pi T)t} - 1}{\delta'/T} \right) dt \quad (\text{A18})$$

and

$$g_1(\delta, \delta') = \frac{\delta'/T}{2(e^{\delta'/T} - 1)} \left[2 \frac{\delta}{T} - \operatorname{Re} \int_0^{\infty} \frac{d}{dt} \left(\frac{e^{-i(\delta/2\pi T)t}}{2 \sinh(\frac{1}{2}t)} \right) \times \left(\frac{\delta'}{T} t + \frac{4\pi^2}{\sinh(\frac{1}{2}t)} \frac{e^{-i(\delta'/2\pi T)t} - 1}{\delta'/T} \right) \right]. \quad (\text{A19})$$

Using (A18) and (A19) in (A12) and (A13), respectively, one obtains, after some manipulations,

$$\Gamma_1(0, \delta) = \frac{\delta/T}{e^{\delta/T} - 1} \left[\ln \frac{2\pi T}{D} + \psi \left(\frac{1}{2} \right) + \phi_1 \left(\frac{\delta}{2\pi T} \right) \right], \quad (\text{A20})$$

$$\Gamma_1(\delta, 0) = \ln \frac{2\pi T}{D} + \psi \left(\frac{1}{2} \right) + \phi_2 \left(\frac{\delta}{2\pi T} \right), \quad (\text{A21})$$

$$G_1(0, \delta) = \frac{(\delta/T)^2}{2(e^{\delta/T} - 1)} \left[\ln \frac{2\pi T}{D} + \psi \left(\frac{1}{2} \right) + \phi_3 \left(\frac{\delta}{2\pi T} \right) \right], \quad (\text{A22})$$

$$G_1(\delta, 0) = \phi_4(\delta/2\pi T), \quad (\text{A23})$$

where

$$\phi_1(x) \equiv \int_0^{\infty} \frac{dt}{2 \sinh(\frac{1}{2}t)} \left(1 - \frac{1}{x} \frac{\sin xt}{2 \sinh(\frac{1}{2}t)} \right), \quad (\text{A24})$$

$$\phi_2(x) \equiv \int_0^{\infty} \frac{dt}{2 \sinh(\frac{1}{2}t)} \left(1 - \frac{t \cos xt}{2 \sinh(\frac{1}{2}t)} \right), \quad (\text{A25})$$

$$\phi_3(x) \equiv \int_0^{\infty} dt \frac{\cosh(\frac{1}{2}t)}{4 \sinh^2(\frac{1}{2}t)} \left(t + \frac{1}{\sinh(\frac{1}{2}t)} \frac{\cos xt - 1}{x^2} \right), \quad (\text{A26})$$

$$\phi_4(x) \equiv \pi \int_0^{\infty} dt \frac{\sin xt}{2 \sinh^2(\frac{1}{2}t)} \left(\frac{t}{2} \coth \frac{t}{2} - 1 \right). \quad (\text{A27})$$

The integrals (A24)–(A27) can then be expressed in terms of $\psi(z)$ and $\psi'(z)$. Starting with

$$\operatorname{Re}\psi(1+ix) = \psi(1) + \int_0^\infty \frac{e^{-t/2}}{2 \sinh(\frac{1}{2}t)} (1 - \cos xt), \quad (\text{A28})$$

it needs some judicious integrations by parts to arrive at the following relations:

$$\phi_1(x) = \operatorname{Re}\psi(1+ix) - \psi(1) + 2 \ln 2 - 1, \quad (\text{A29})$$

$$\phi_2(x) = \phi_1(x) + x \frac{d}{dx} \operatorname{Re}\psi(1+ix), \quad (\text{A30})$$

$$\phi_3(x) = \frac{1}{2} + \phi_1(x), \quad (\text{A31})$$

$$\phi_4(x) = \pi x \left(1 - x \frac{d}{dx} \operatorname{Re}\psi(1+ix) \right). \quad (\text{A32})$$

However, since

$$\operatorname{Re}\psi(1+ix) = \operatorname{Re}\psi(ix) \quad (\text{A33})$$

and

$$\psi(\frac{1}{2}) = \psi(1) - 2 \ln 2, \quad (\text{A34})$$

if we substitute (A29)–(A32) into Eqs. (A20)–(A23), we finally obtain

$$\Gamma_1(0, \delta) = \frac{\delta/T}{e^{\delta/T} - 1} \left[\ln \frac{2\pi T}{D} + \operatorname{Re}\psi\left(i \frac{\delta}{2\pi T}\right) - 1 \right], \quad (\text{A35})$$

$$\Gamma_1(\delta, 0) = \ln \frac{2\pi T}{D} + \operatorname{Re}\psi\left(i \frac{\delta}{2\pi T}\right) - 1 - \frac{\delta}{2\pi T} \operatorname{Im}\psi'\left(i \frac{\delta}{2\pi T}\right), \quad (\text{A36})$$

$$G_1(0, \delta) = \frac{(\delta/T)^2}{2(e^{\delta/T} - 1)} \left[\ln \frac{2\pi T}{D} + \operatorname{Re}\psi\left(i \frac{\delta}{2\pi T}\right) - \frac{1}{2} \right], \quad (\text{A37})$$

$$G_1(\delta, 0) = \frac{\delta}{2T} \left[1 + \frac{\delta}{2\pi T} \operatorname{Im}\psi'\left(i \frac{\delta}{2\pi T}\right) \right]. \quad (\text{A38})$$

The expressions (A35)–(A38) are then used to com-

pute the thermoelectric power given by (32).

APPENDIX B

We present here the analytical calculation of the thermoelectric power in the case of two levels split by the CF effect. We use the notations of Secs. III and IV and also the following ones:

$$p_+ = p_{21}, \quad p_- = p_{12},$$

$$\lambda_+ = \lambda_{12}, \quad \lambda_- = \lambda_{21},$$

$$\Delta = \Delta_{21},$$

$$\delta_+ = \Delta_{12}^0 = -\Delta_{21}^0 = -\delta_-.$$

$$\lambda_{\pm} = \frac{1}{2} \pm \frac{1}{2} \left((p_{21} - p_{12})^2 + 4 \frac{d_{21}}{A} (2p_{12} - 1) \right)^{1/2},$$

$$a \equiv 2\alpha_1\alpha_2 J_{12}^2 [\alpha_2 J_{22} \langle n_2 \rangle - \alpha_1 J_{11} \langle n_1 \rangle + (V_{22} + V_{11}) (\langle n_1 \rangle - \langle n_2 \rangle)],$$

$$b \equiv 2\alpha_1\alpha_2 J_{12}^2 \langle n_1 \rangle (\alpha_2 J_{22} - \alpha_1 J_{11}),$$

$$\mu \equiv \frac{\gamma p_+ (2p_- - 1)}{\lambda_+ - \lambda_-},$$

where

$$\gamma = \alpha_1\alpha_2 J_{12}^2 \langle n_1 \rangle / A,$$

$$d \equiv 2\mu [1 + \mu / (\lambda_+ - \lambda_-)],$$

$$A = 6\mathfrak{U}^2 + \alpha_1 \langle n_1 \rangle (\alpha_1 - \langle n_1 \rangle) J_{11}^2 + \alpha_2 \langle n_2 \rangle (\alpha_2 - \langle n_2 \rangle) J_{22}^2,$$

if we take \mathfrak{U} for the assumed common value of \mathfrak{U}_{11} and \mathfrak{U}_{22} .

Then, the Seebeck coefficient in the case of two levels is exactly given by

$$S = (k_B/e)n(\epsilon_F)\rho \left\{ -aG_1(\Delta, 0) + b[G_1(0, \Delta) - \beta\Delta\Gamma_1(0, \Delta)] - c_+[G_1(\Delta - \delta_+, 0) - \beta\delta_+\Gamma_1(\Delta - \delta_+, 0)] - (c_+ - c_-)[G_1(\delta_+, 0) + \beta\delta_+\Gamma_1(\delta_+, 0)] - c_-[G_1(\Delta + \delta_+, 0) + \beta\delta_+\Gamma_1(\Delta + \delta_+, 0)] + h_+[G_1(0, \Delta - \delta_+) - \beta\Delta\Gamma_1(0, \Delta - \delta_+)] - h_-[G_1(0, \Delta + \delta_+) - \beta\Delta\Gamma_1(0, \Delta + \delta_+)] + \kappa G_1(0, \delta_+) \right\},$$

where

$$\rho = 1/[A(1 - 2\mu\beta\delta_+)], \quad c_+ = \frac{\mu^2}{\lambda_+(\lambda_+ - 1)} \left(a - b \frac{p_+}{p_+ - \lambda_+} \right), \quad c_- = \frac{\mu^2}{\lambda_-(\lambda_- - 1)} \left(a - b \frac{p_+}{p_+ - \lambda_-} \right),$$

$$h_+ = \frac{p_+ - \lambda_+}{\lambda_- p_+} (ad - \Sigma_+ bp_+), \quad h_- = \frac{p_+ - \lambda_-}{\lambda_+ p_+} (ad - \Sigma_- bp_+), \quad \kappa = \frac{p_+}{\lambda_+} b,$$

with

$$\Sigma_+ = \left(d - \frac{\mu^2}{p_+ - \lambda_+} \right) \frac{1}{p_+ - \lambda_+}, \quad \Sigma_- = \Sigma_+ - 1.$$

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