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Thermal conductivity of cerium compounds

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The third-order perturbation-theory thermal conductivity is computed in the framework of the effective exchange Hamiltonian which describes both the resonant-scattering character and the crystalline field effect of cerium. The model is applied to the thermal conductivity measurements of cerium compounds and good agreement is found for $CeAl_2$ and $CeCu_2Si_2$.

I. INTRODUCTION

Cerium compounds have been extensively studied in recent years and most of their properties have been experimentally measured and theoretically computed. In particular, the properties of cerium alloys or compounds, which present a Kondo effect, have been successfully analyzed in the framework of the effective exchange Hamiltonian which describes the large resonant scattering due to cerium and takes into account the crystalline-field effect.[1,2] Third-order calculations of the electrical resistivity,[2] magnetoresistivity,[3] Hall effect,[4] thermoelectric power,[5] and relaxation rate[6,7] have been performed for cerium (or ytterbium) Kondo alloys or compounds, and the purpose of the present paper is to compute the thermal conductivity due to electrons in the same framework.

The thermal conductivity and the Lorenz ratio have been recently measured in several Kondo cerium alloys and compounds. Figure 1 shows the temperature dependence of the thermal conductivity of CeB_6 (Ref. 8), $CeCu_6$ (Ref. 9), $CeAl_2$ (Refs. 10 and 11), $CeCu_2$ (Ref. 12), and $CeCu_2Si_2$ (Ref. 13). The thermal conductivity has been measured in the case of Kondo alloys, such as $Ce_xLa_{1-x}Cu_6$ (Ref. 14) or dilute $(LaCe)Al_2$ (Ref. 15). The experimental curves of the thermal conductivity show a general increase with temperature, with either an inflection point between 50 and 100 K as in $CeCu_6$ and $CeAl_2$, or a flattening in the same temperature range in $CeCu_2$ or even a very broad maximum at roughly 50 K in $CeCu_2Si_2$.

The experimental values of the reduced Lorenz number L/L_0 have been also measured for cerium Kondo compounds. The Lorenz number L is defined here by

$$L = \frac{K\rho}{T} , \tag{1}$$

where K is the thermal conductivity and ρ the electrical resistivity. The Sommerfeld value L_0 of the Lorenz number is equal to $L_0 = 2.45 \times 10^{-8}\ \mathrm{W\,\Omega\,K^{-2}}$. The Lorenz number of the two compounds CeB_6 (Ref. 8) and $CeCu_6$ (Ref. 9), which have a very large magnetic Kondo resistivity, reaches a very large value, of order $5\,L_0$, at low temperatures. Similarly, the Lorenz number is also larger than L_0 in $CeAl_2$ (Ref. 10) or $Ce_xLa_{1-x}Cu_6$ alloys,[14] but lies between $2L_0$ and $4L_0$ at low temperatures. On the contrary, the Lorenz number of $CeCu_2$ is smaller and close to L_0 from 30 to 300 K (Ref. 12). In all the preceding cases, the experimental value of the Lorenz number is determined by taking in Eq. (1) the total values of K and ρ, i.e., including both the phonon and the electron contributions.

Let us now study the origin of the thermal conductivity in such cerium compounds. The thermal conductivity of both LaB_6 and $LaCu_6$ is much larger than that of CeB_6 and $CeCu_6$, respectively. It results that both the thermal and electrical resistivities of these two cerium compounds are much larger than those of the two equivalent nonmagnetic lanthanum compounds in the low-temperature domain up to at least 100 K. Moreover, we can reasonably think that the phonon contribution to the thermal resistivity of cerium compounds is approximately the

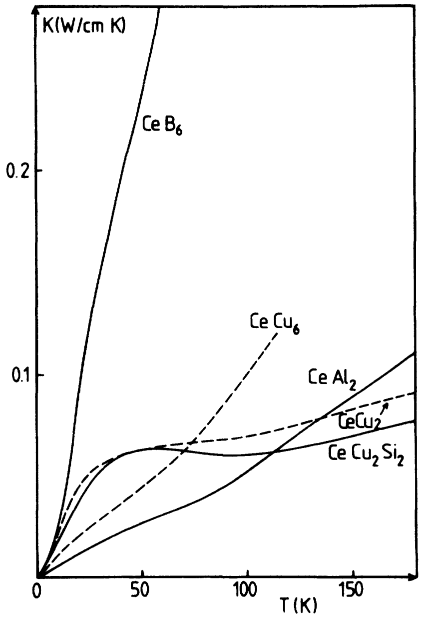

FIG. 1. Experimental curves of the thermal conductivity K (in W/cm K) plotted vs temperature for several cerium compounds.

same as the thermal resistivity itself of the equivalent lanthanum compounds, although this approximation is certainly less valid in principle for the thermal resistivity than for the electrical resistivity. Thus, in contrast to the previous idea of Peysson *et al.*[8–10] that the thermal conductivity was mainly due to phonons above 5 K in CeB_6 and $CeCu_6$, we assume that the thermal conductivity of cerium Kondo compounds has a magnetic origin arising from the Kondo effect of cerium, as previously established for the electrical resistivity[2] or the thermoelectric power.[5]

We will, therefore, compute in this paper the thermal conductivity in the framework of the effective resonant-scattering Hamiltonian appropriate for the study of the Kondo effect in cerium compounds.

II. THE THEORETICAL MODEL

We shall compute here the thermal conductivity K in the third order of perturbation with the effective resonant-scattering Hamiltonian. We shall use, therefore, the third-order calculations and, in particular, the relaxation time, which have already been derived in Ref. 2 for the resistivity and in Ref. 5 for the thermoelectric power; in the following, we use the same notations as in Refs. 2 and 5.

The effective resonant-scattering Hamiltonian for a cerium impurity in a metallic host can be written as

$$\begin{aligned} H = & \sum_{k,M} \varepsilon_k n_{kM} + \sum_{M} E_M n_M \\ & - \sum_{\substack{k,k' \\ M,M'}} J_{MM'} C^*_{k'M'} C_{kM} (C^*_M C_{M'} - \delta_{MM'} \langle n_M \rangle) \\ & + \sum_{k,k',M} \mathcal{V}_{MM} C^*_{k'M} C_{kM} , \end{aligned} \tag{2}$$

with the usual notations and definitions of Refs. 2 and 5: C^*_{kM} represents the creation operator of a conduction electron of energy ε_k in the partial-wave state M (defined by the quantum numbers $l=3$, $s=\frac{1}{2}$, $j=\frac{5}{2}$, and $j_z=M$), while C^*_M represents the creation operator of a localized $4f$ electron in the state M of the Ce atom. M denotes, as usual, the quantum number characterizing an eigenstate of energy E_M in the presence of the crystalline field (CF), i.e., either any state of the doublet Γ_7 or the quartet Γ_8 for cubic symmetry (as in $CeAl_2$), or any eigenvalue $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, or $\pm\frac{5}{2}$ for hexagonal or tetragonal symmetry (as in $CeCu_2Si_2$). The energies ε_k and E_M are defined with respect to the Fermi energy. The exchange integrals are given by

$$J_{MM'} = \frac{|V_{kF}|^2}{2} \left[\frac{1}{E_M} + \frac{1}{E_{M'}} \right] , \tag{3}$$

defined with a cutoff D. In Eq. (3), V_{kF} is the hybridization parameter between $4f$ and conduction electrons. The $\mathcal{V}_{MM}$ parameters, which represent pure direct scattering, are all taken equal to a common value $\mathcal{V}$.

With the Hamiltonian (2), we follow the Kondo approach of calculating the scattering amplitude in the second Born approximation. The scattering probability is then calculated up to the third order in $J_{MM'}$ and $\mathcal{V}$. This calculation has been presented in Refs. 2 and 5 and here we simply give the main results. The relaxation time τ_k of a conduction electron is given by

$$\frac{1}{\tau_k} = \frac{mkv_0c}{\pi\hbar^3(2j+1)} (R_k + S_k) , \tag{4}$$

where m is the mass of the electron, k its wave number, v_0 the sample volume, c the concentration of cerium atoms, and $2j+1=6$ the degeneracy of the $4f^1$ configuration of cerium. R_k and S_k, respectively, denote the second- and third-order terms and are given by expressions (38) and (39) of Ref. 2.

In the usual third-order approximation where the third-order term S_k is assumed to be much smaller than the second-order one R_k, we write, as in Refs. 2 and 5, the relaxation time as

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

Indeed, the approximation of inverting $1/\tau_k$, i.e., of passing from Eq. (4) to Eq. (5), is valid only if the third-order term S_k is much smaller than the second-order one R_k; in other words, the approximation is valid for temperatures higher than the corresponding Kondo temperature. The ratio of the third- and second-order terms, which has been computed in the case of the magnetic resistivity,[2] was there found smaller than 1, although not really much smaller than 1, except at very low temperatures for zero or small $\mathcal{V}$ values. But, Guessous and Matho[16] have recently computed the transport properties up to fourth order in $J_{MM'}$ by using a different approximation which consists in taking an analytical form for the relaxation time and adjusting it by comparison with numerical calculations. They have shown that the approximation of inverting $1/\tau_k$ is questionable in the calculation of the thermoelectric power when $\mathcal{V}=0$.

However, the essential physical features are well described in most cases by this approximation of passing from Eq. (4) to Eq. (5), even if S_k is smaller than R_k, but not always much smaller. We shall, therefore, use this approximation in the following calculation of the thermal conductivity by taking care that the third-order term is clearly smaller than the second-order one.

According to the previous calculation of the resistivity,[2] the validity of the perturbation theory is, indeed, extended when the Kondo temperature decreases, which is obtained here in the presence of a crystalline field, for a larger $\mathcal{V}$ value or a smaller effective degeneracy of the occupied levels (for example, the perturbation theory is much more valid for a doublet ground state than for a quartet).

Let us now write the classical formulas for the transport properties. The thermal conductivity K is given by

$$K = \frac{1}{T} \left[K_2 - \frac{(K_1)^2}{K_0} \right] , \tag{6}$$

while the thermoelectric power S and the electrical conductivity $\sigma = 1/\rho$ are given by

$$S = -\frac{K_1}{|e|\,TK_0} , \tag{7}$$

$$\sigma = e^2 K_0 , \tag{8}$$

where the integrals K_n are given by

$$K_n = \frac{k_F^3}{3\pi^2 m} \int \varepsilon_k^n \tau(\varepsilon_k) \left[-\frac{\partial f_k}{\partial \varepsilon_k} \right] d\varepsilon_k . \tag{9}$$

In the perturbation theory up to third order in $J_{MM'}$ and $\mathcal{V}$, the lowest terms of S and $\rho = 1/\sigma$ are, respectively, of the third and second order, so that the second term of Eq. (6) is at least of the fourth order and can be completely neglected in our present calculation. Moreover, when we compute the integral K_2, we take the value k_F for k, which is slowly varying around the Fermi energy with respect to the other functions entering τ_k.

Thus, it results that the thermal conductivity K can be written as

$$K = \frac{(2j+1)\hbar^3 k_F^2}{3\pi m^2 v_0 c} \frac{1}{T} (W_2 - W_3) , \tag{10}$$

with

$$W_2 = \int \varepsilon_k^2 \left[-\frac{\partial f_k}{\partial \varepsilon_k} \right] \frac{d\varepsilon_k}{R_k} , \tag{11}$$

$$W_3 = \int \varepsilon_k^2 \left[-\frac{\partial f_k}{\partial \varepsilon_k} \right] \frac{S_k}{R_k^2} d\varepsilon_k , \tag{12}$$

where f_k is the Fermi-Dirac distribution function. The method to compute the thermal conductivity is similar to the methods used for the resistivity in Ref. 2 and for the thermoelectric power in Ref. 5, except that here we have a ε_k^2 term in the integrals (11) and (12).

We, therefore, define the following integrals:

$$B(\delta) = \int_{-\infty}^{+\infty} \varepsilon_k^2 \left[-\frac{\partial f_k}{\partial \varepsilon_k} \right] \frac{d\varepsilon_k}{[1 - f_k(1 - e^{\beta\delta})]} , \tag{13}$$

$$\mathcal{C}_n(\delta, \delta') = \int_{-\infty}^{+\infty} \varepsilon_k^2 \left[-\frac{\partial f_k}{\partial \varepsilon_k} \right] \frac{g(\varepsilon_k + \delta) d\varepsilon_k}{[1 - f_k(1 - e^{\beta\delta'})]^n} , \tag{14}$$

with $\beta = 1/(k_B T)$ and

$$g(\varepsilon) = \sum_q \frac{f_q - \frac{1}{2}}{\varepsilon_q - \varepsilon} \tag{15}$$

is the usual function appearing in the Kondo problem.

We use here, as in Refs. 2 and 5, indices representing the CF energy levels rather than the eigenstates: let i $(=1,2,3,\ldots,)$ denote the energy level E_i of degeneracy α_i and of the thermal average of the occupation number $\langle n_i \rangle$ for the localized electron in each state M at the energy E_i. Also, $\Delta_{ij} = E_i - E_j$. Then, from Ref. 2 and expression (22) of Ref. 5, it results that W_2 is equal to

$$W_2 = \frac{B(0)}{A} + \frac{1}{A} \sum_{\substack{i,j \\ (i \neq j)}} \frac{\mu_{ij}}{\lambda_{ij}} B(\Delta_{ij}^0) , \tag{16}$$

where

$$A = \sum_i \alpha_i \left[\mathcal{V}_{ii}^2 + \alpha_i J_{ii}^2 \langle n_i \rangle \left(1 - \frac{\langle n_i \rangle}{\alpha_i} \right) \right] . \tag{17}$$

λ_{ij} are the roots of the equation $R_k(f_k) = 0$ with the coefficients μ_{ij}, as explained in expressions (60)–(66) of Ref. 2, and the energies Δ_{ij}^0 are defined by

$$\lambda_{ij} = \frac{1}{1 - e^{\beta\Delta_{ij}^0}} . \tag{18}$$

Then, the calculation of W_3 is strictly similar to that of $eT\sigma^{(2)}S$ given by expression (20) of Ref. 5, except that ε_k is changed to ε_k^2 in the integral on ε_k.

It results that W_3 is equal to

$$\begin{aligned} W_3 = {} & \frac{1}{A^2} \sum_{i,l} C_i^l \mathcal{C}_1^l(\Delta_{li}, 0) \\ & + \frac{1}{A^2} \sum_{\substack{n,n' \\ (n \neq n')}} \sum_{i,l} [U_{nn'}^{il} \mathcal{C}_1(\Delta_{li}, \Delta_{nn'}^0) \\ & + V_{nn'}^{il} \mathcal{C}_2(\Delta_{li}, \Delta_{nn'}^0)] . \end{aligned} \tag{19}$$

The coefficients C_i^l, $U_{nn'}^{il}$, and $V_{nn'}^{il}$, which are of third order in J_{ij} and $\mathcal{V}_{ii}$, depend on the different parameters α_i, $\langle n_i \rangle$, Δ_{ij}, J_{ij}, and $\mathcal{V}_{ii}$. They are, respectively, given by expressions (15), (33), and (34) of Ref. 5 on the thermoelectric power.

Finally, Eqs. (10), (16), and (19) give the third-order expression of the thermal conductivity that we shall compute in Sec. III.

III. CALCULATION OF THE THERMAL CONDUCTIVITY

We compute here the thermal conductivity for the cases of two or three levels split by the crystalline field. In the case of three levels, the roots λ_{ij} and the corresponding coefficients μ_{ij} have to be determined numerically, and finally the calculation rapidly becomes very complex. Thus, for the sake of simplicity, we will use in the following 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 $\frac{1}{2}$. Moreover, we have seen, in the cases of the resistivity[2] and thermoelectric power,[5] that the $f_k = \frac{1}{2}$ approximation does not modify the temperature variation of the transport properties and changes their values only a little in the domain of intermediate temperatures.

So, within this approximation, we write

$$R_k(f_k = \tfrac{1}{2}) = R = A + \sum_{\substack{i,j \\ (i \neq j)}} \frac{2\alpha_i \alpha_j J_{ij}^2 \langle n_j \rangle}{1 + e^{\beta\Delta_{ij}}} , \tag{20}$$

$$S_k(f_k = \tfrac{1}{2}) = \sum_{i,l} \gamma_i^l g(\varepsilon_k + \Delta_{li}) , \tag{21}$$

with

$$\gamma_i^l = C_i^l + \sum_{j(\neq i)} \frac{4 J_{ij} J_{il} J_{jl} \alpha_i \alpha_j \alpha_l \langle n_j \rangle}{1 + e^{\beta\Delta_{ij}}} . \tag{22}$$

A and $g(\varepsilon_k)$ are given, respectively, by (17) and (15); C_i^l is given by expression (15) of Ref. 5.

After integration, the two integrals W_2 and W_3 defined by, respectively, (11) and (12), are given, within the $f_k=\frac{1}{2}$ approximation, by

$$W_2=\frac{\pi^2}{3}\frac{(k_BT)^2}{R} \tag{23}$$

and

$$W_3=\frac{\pi^2}{3}n(E_F)\frac{(k_BT)^2}{R^2}\sum_{i,l}\gamma_i^l I(\Delta_{li}) , \tag{24}$$

where the function $I(\delta)$ is defined by

$$I(\delta)=\ln\frac{2\pi T}{D}+\psi(\tfrac{1}{2})+\varphi_5\left[\frac{\delta}{2\pi T}\right] . \tag{25}$$

The function $\varphi_5(x)$ is given by

$$\varphi_5(x)=\int_0^\infty\frac{dt}{2\sinh\frac{t}{2}}\left[1-\frac{3\cos xt}{\sinh\frac{t}{2}}\left[\frac{4\sinh t-t(3+\cosh t)}{4\sinh^2\frac{t}{2}}\right]\right] \tag{26}$$

and

$$\psi(\tfrac{1}{2})=\psi(1)-2\ln 2=-1.9635 . \tag{27}$$

It results finally that the thermal conductivity K is given by

$$K=\frac{(2j+1)\pi k_F^2\hbar^3k_B^2}{9m^2v_0c}\frac{T}{R}(1-Y) , \tag{28}$$

where the function Y, which is the ratio of the third- and second-order terms is given by

$$Y=\frac{n(E_F)}{R}\sum_{i,l}\gamma_i^l I(\Delta_{li}) . \tag{29}$$

Indeed, Y must be much smaller than 1 in order that the perturbation theory be valid. We will study in the following the temperature dependence of Y, especially at low temperatures, and we will show that Y must diverge for T tending to zero. It results that there exists a critical "Kondo temperature" T_k, below which Y becomes larger than 1, and the present perturbative model must be valid only for temperatures much higher than this critical temperature defined here for the calculation of the thermal conductivity.

Let us compute now the function $\varphi_5(x)$ defined by Eq. (26). In our paper on the thermoelectric power,[5] we have computed four similar functions called $\varphi_i(x)$ (with $i=1$, 2, 3, and 4). Using, as previously,[5] some judicious integrations by parts, we express $\varphi_5(x)$ in terms of the digamma function $\psi(z)$ as follows:

$$\varphi_5(x)=2\ln 2-\psi(1)-\tfrac{1}{3}-4x^2+\mathrm{Re}\psi(1+ix)+x(1+4x^2)\frac{d}{dx}[\mathrm{Re}\psi(1+ix)] , \tag{30}$$

where $\psi(1)$ is given by (27).

Let us now study the low-temperature dependence of $I(\Delta_{li})$ and Y. First of all, the value $I(0)$ of the function given by (25) for $\delta=0$ is equal to

$$I(0)=\ln\frac{2\pi T}{D}+\psi(\tfrac{1}{2})+2\ln 2-\tfrac{1}{3} , \tag{31}$$

and has a logarithmic behavior at low temperatures.

Then, we calculated the asymptotic expansion of $I(\delta)$ for T tending to zero and a finite δ value, i.e., for $k_BT \ll \delta$, and we found

$$I(\delta)\sim\ln\left|\frac{\delta}{D}\right|-\frac{13}{60}\left[\frac{2\pi T}{\delta}\right]^2-\frac{1}{40}\left[\frac{2\pi T}{\delta}\right]^4+\cdots . \tag{32}$$

In the limiting case $k_BT\to 0$, i.e., k_BT is much smaller than the lowest crystalline-field splitting, only the ground state, labeled by $i=1$ with a degeneracy α_1 and a thermal average $\langle n_1\rangle=1/\alpha_1$, is occupied. If we take all the direct scattering parameters $\mathcal{V}_{ii}$ equal to a common value $\mathcal{V}$ and call J_{11} the exchange integral for the ground state, the low-temperature limit of R, given by (20) in the $f_k=\frac{1}{2}$ approximation, is equal to

$$R=(2j+1)\mathcal{V}^2+|J_{11}|^2\frac{(\alpha_1^2-1)}{\alpha_1} . \tag{33}$$

The different excited levels (labeled by the index j) lie at a distance Δ_{j1} above the ground state. α_j and J_{j1} correspond, respectively, to the degeneracy of the level j and the exchange integral (3) with M in the ground state and M' in the level j. Since the function $\dot{I}(\delta)$ is an even function of δ, we obtain for the low-temperature limit of Y

$$Y=\frac{n(E_F)}{R}\left[2J_{11}^3(\alpha_1^2-1)\left[\ln\frac{2\pi T}{D}+\psi(\tfrac{1}{2})+2\ln 2-\tfrac{1}{3}\right]+2\sum_j J_{11}|J_{1j}|^2\frac{\alpha_j}{\alpha_1}(\alpha_1^2-1)\ln\left|\frac{\Delta_{j1}}{D}\right|\right] . \tag{34}$$

Thus, Y has a logarithmic behavior at low temperatures and Y becomes larger than 1 at a critical temperature T_k defined by

$$k_B T_k = D_0 \exp\left[-\left[1+\frac{\mathcal{V}^2}{|J_{11}|^2}\frac{(2j+1)\alpha_1}{\alpha_1^2-1}\right]\Big/[2\alpha_1 n(E_F)|J_{11}|]\right] . \tag{35}$$

The cutoff D_0 is a function of the previously defined cutoff D and of the parameters used here, and is given by[17]

$$\ln\left|2.49\frac{D}{2\pi D_0}\right| = \sum_j \frac{\alpha_j}{\alpha_1}\left|\frac{J_{1j}}{J_{11}}\right|^2 \ln\left|\frac{\Delta_{j1}}{D}\right| . \tag{36}$$

Let us now compare expressions (35) and (36) to the similar expressions previously obtained for the resistivity.[2] If we take the same definition of T_k, i.e., the temperature corresponding to equal values of the second- and third-order terms, the ratio $k_B T_k / D_0$ of the Kondo temperature to the effective cutoff is exactly the same as the similar value obtained for the resistivity. Moreover, after correcting a minor error in Ref. 2,[17] the dependence on α_i, J_{1i}, and Δ_{i1} of the effective cutoff D_0 is the same as that given for the resistivity, except for a small change of the numerical coefficient in front of D/D_0.

IV. THEORETICAL RESULTS FOR THE THERMAL CONDUCTIVITY

We now present in Figs. 2 and 3 some typical theoretical curves for the thermal conductivity K of cerium compounds. In Fig. 2 we show the variation of K with J_{11} and $\mathcal{V}$, while, in Fig. 3, we present theoretical curves corresponding to different crystal-field level schemes.

All the theoretical curves shown in Figs. 2 and 3 are computed by taking a density of states of the conduction band at the Fermi energy for one spin direction $n(E_F)=2$ states/eV atom, a cutoff $D=850$ K, and a hybridization parameter $V_{kf}=0.07$ eV. Moreover, in order to derive the numerical coefficient of K in expression (28), we take the atomic volume $v_0=234$ a.u. of $\mathrm{CeAl_2}$ and three electrons per atom,[2] so that $k_F = 1.37\times 10^8\ \mathrm{cm}^{-1}$ in the free-electron approximation. We choose also $(2j+1)=6$, $m=1$ in a.u. and $c=1$. More appropriate values of m and c will be taken in Fig. 6 for comparison with experiment.

Figure 2 shows theoretical curves for a cubic crystalline field with a Γ_7 ground state and a splitting $\Delta=100$ K. Four curves are plotted with $\mathcal{V}=-0.25$ eV and increasing values of $|J_{11}|$, and the last one is plotted with $\mathcal{V}=-0.5$ eV and $J_{11}=-0.1$ eV. We see that the two curves plotted, respectively, for $J_{11}=-0.05$ eV, $\mathcal{V}=-0.25$ eV and for $J_{11}=-0.1$ eV, $\mathcal{V}=-0.5$ eV behave almost linearly versus temperature; these curves

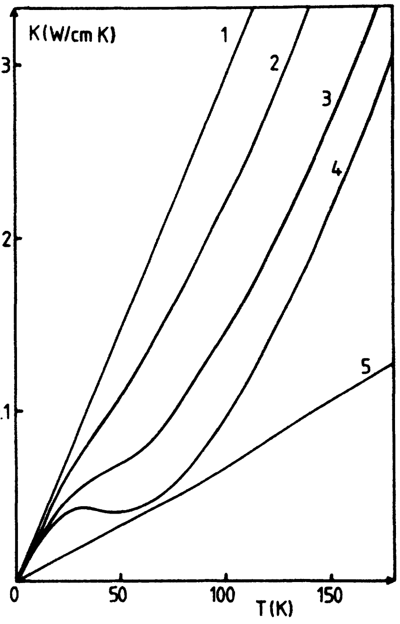

FIG. 2. Theoretical plots of the thermal conductivity K (in W/cm K) vs temperature for a cubic crystalline field with a Γ_7 ground state and a splitting $\Delta=100$ K, a density of states $n(E_F)=2$ states/eV atom, $D=850$ K, $V_{kf}=0.07$ eV and different values of J_{11} and $\mathcal{V}$: Curve 1 corresponds to $J_{11}=-0.05$ eV, $\mathcal{V}=-0.25$ eV; curve 2 to $J_{11}=-0.08$ eV, $\mathcal{V}=-0.25$ eV; curve 3 to $J_{11}=-0.1$ eV, $\mathcal{V}=-0.25$ eV; curve 4 to $J_{11}=-0.11$ eV, $\mathcal{V}=-0.25$ eV, and curve 5 to $J_{11}=-0.1$ eV, $\mathcal{V}=-0.5$ eV.

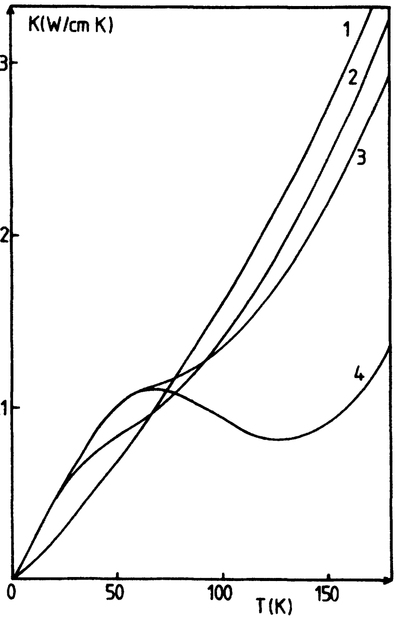

FIG. 3. Theoretical plots of the thermal conductivity K (in W/cm K) vs temperature for a density of states $n(E_F)=2$ states/eV atom, $D=850$ K, $V_{kf}=0.07$ eV, $J_{11}=-0.1$ eV, $\mathcal{V}=-0.25$ eV, and the following crystalline-field schemes: Curve 1 corresponds to cubic field with a Γ_8 ground state and a splitting $\Delta=200$ K; curve 2 to a hexagonal field with three doublets at energies 0, 100, and 200 K; curve 3 to a cubic field with a Γ_7 ground state and a splitting $\Delta=200$ K; curve 4 to a hexagonal field with three doublets at 0, 200, and 400 K.

correspond to the case where the third-order term is much smaller than the second-order one and, according to (28), K is almost linear in T. On the other hand, the "inflection" of the curve increases with increasing $|J_{11}|$, to finally reach a curve with a maximum and a minimum at roughly $\Delta/2$ for a large value $|J_{11}|=0.11$ eV.

This behavior can be well understood in the preceding theoretical analysis. The second-order term R decreases when $|J_{11}|$ or $\mathcal{V}$ decrease. Thus, when $\mathcal{V}$ increases with all the other parameters kept constant, both $1/R$ and Y decrease, and it results that both K and the inflection of K decrease. On the other hand, when $|J_{11}|$ is increased, keeping all the other parameters constant, $1/R$ decreases, Y increases, but Y/R decreases; it results that the value of K decreases but the curve has a more pronounced inflection and departs more and more from the second-order linear behavior.

Figure 3 shows some other theoretical curves obtained with fixed values of $J_{11}=-0.1$ eV, and $\mathcal{V}=-0.25$ eV, and different crystalline-field schemes. We see that the three curves corresponding to a doublet ground state start together and behave linearly at low temperatures; then they depart from this law at a temperature of order $\Delta/4$, where Δ is the distance of the first excited state from the ground state. Then, at higher temperatures, there is an important change of slope with temperature and all the curves again have a linear behavior at high temperatures. On the contrary, in the cubic case with a Γ_8 ground state, the thermal conductivity increases continuously with increasing temperature and the crystalline-field effect does not appear to play an important role for the thermal conductivity, as theoretically expected and previously observed for the resistivity.[2,3] We can finally notice that all the curves have almost a linear behavior at high temperatures because the third-order term becomes much smaller than the second-order one in this temperature domain. On the contrary, we obtain curves with two extrema when the third-order term becomes relatively large, although, indeed, always smaller than the second-order term.

Figure 4 gives the theoretical plots of Y versus temperature for the sets of parameters corresponding to the curves of Fig. 3. However, we have not plotted Y at very low temperatures (typically smaller than 10 K), where Y becomes rapidly much larger than 1, and where the perturbation theory is no longer valid. In all the cases shown on Figs. 2 and 3, Y, although not always much smaller than 1, remains smaller than 1. At high temperatures, Y is very small, which yields an almost linear dependence of K on temperature, as already shown in Figs. 2 and 3.

In general, Y increases and consequently the validity of the perturbation theory decreases when $|J_{11}n(E_F)|$ increases and $\mathcal{V}$ decreases, as previously noticed.[2,5] In particular, the perturbation theory would not be valid for $\mathcal{V}=0$ with the choice of other parameters used, for instance in Fig. 3. The condition $Y<1$ is particularly critical here since the thermal conductivity is proportional to $1-Y$, but the same condition must be checked for the calculation of resistivity[2] and thermoelectric power.[5] In particular, we have to note here that the curves of the thermoelectric power computed with $\mathcal{V}=0$ in Ref. 5 are not correct, since the perturbation theory is no longer valid; this point was also noticed by Guessous and Matho.[16]

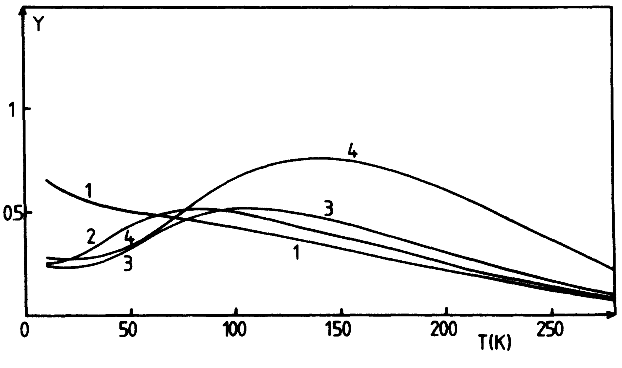

FIG. 4. Theoretical plots of Y, the ratio of the third- and second-order terms, vs temperature for the same sets of parameters and the same labels for the different curves as those used in Fig. 3.

Figure 5 shows the temperature dependence of the reduced Lorenz number L/L_0 defined by (1) for the same sets of parameters as those used for the curves of Fig. 3. As in Fig. 4, we have not plotted L/L_0 at very low temperatures where the perturbation theory is no longer valid. The essential result, shown by the plots of Fig. 5, is that the Lorenz number L remains relatively close to its Sommerfeld value L_0 in the whole temperature domain of Fig. 5. In particular, L is very close to L_0 at low temperatures, and we cannot explain large values of the reduced Lorenz number L/L_0 as experimentally observed in some cerium compounds at low temperatures.

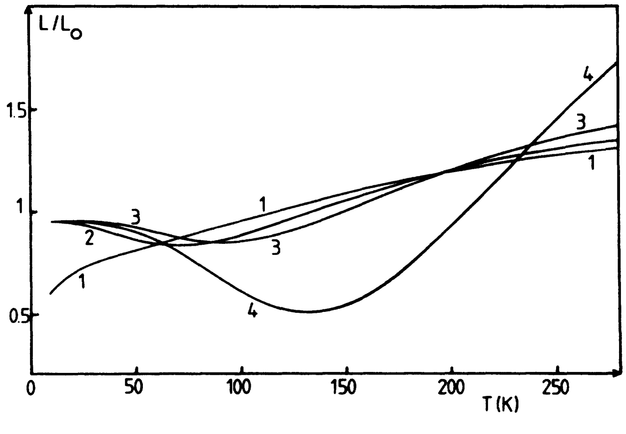

FIG. 5. Theoretical plots of the reduced Lorenz number L/L_0 vs temperature for the same sets of parameters and the same labels for the different curves as those used in Fig. 3.

V. COMPARISON WITH EXPERIMENT AND CONCLUSION

The thermal conductivity of cerium compounds, for example CeB_6 or $CeCu_6$, is much smaller than that of the equivalent nonmagnetic lanthanum compounds. As already explained in the Introduction, we can reasonably deduce that the thermal resistivity of cerium compounds has a magnetic origin due to the Kondo effect and can be accounted for by the present model.

Figure 6 shows a tentative comparison between the experimental and theoretical curves of the thermal conductivity for $CeAl_2$ and $CeCu_2Si_2$ compounds. Both the theoretical curves are obtained by taking the following set of parameters: $n(E_F)=2.2$ states/eV atom, $D=850$ K, $V_{kf}=0.07$ eV, $J_{11}=-0.1$ eV, $\mathcal{V}=-0.24$ eV. We take the cubic symmetry with Γ_7 ground state, and splitting $\Delta=100$ K for the case of $CeAl_2$ and three doublets at energies 0, 140, and 360 K (referred to the ground-state energy) for the case of $CeCu_2Si_2$, as experimentally established by neutron scattering.[18] Finally, we determine the value of the effective mass m by matching the theoretical K value at 100 K to the experimental one; we thus obtain $m=2.72$ for $CeAl_2$ and $m=3.32$ for $CeCu_2Si_2$. All the parameters used for the theoretical curves of Fig. 6 are quite reasonable and agree with previously used theoretical values, in particular those used to fit the resistivity of $CeAl_2$.[2] However, we must be careful in comparing the theoretical calculations since we have adjusted the curves at 100 K. We can see that the fit is very good for $CeAl_2$ and good only up to 120 K for $CeCu_2Si_2$.

Thus, we have obtained reasonable fits for the thermal conductivity of $CeAl_2$ and $CeCu_2Si_2$ with roughly the same parameters as those previously used for fitting their resistivities. Similar fits could also be obtained for the thermal conductivities of $CeCu_6$ and $CeCu_2$. However, it would be rather difficult to fit the large thermal conductivity of CeB_6 by taking the parameters previously used to fit its large electrical resistivity.[3]

The effective resonant-scattering Hamiltonian including crystal-field splitting was used previously to compute the electrical resistivity[2] and thermoelectric power[5] within a perturbation framework. The same model has been employed here to calculate the electronic contribution to the thermal conductivity. Comparison with experimental data shows reasonable agreement for all the three transport coefficients in many cerium compounds over a wide range of temperature.

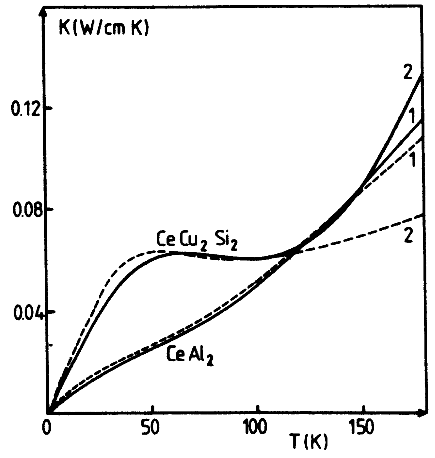

FIG. 6. Comparison between theoretical curves (full lines) and experimental curves (dashed lines) for $CeAl_2$ (curves 1) and $CeCu_2Si_2$ (curves 2) compounds. The theoretical curves are computed for $n(E_F)=2.2$ states/eV atom, $D=850$ K, $V_{kf}=0.07$ eV, $J_{11}=-0.1$ eV, $\mathcal{V}=-0.24$ eV, and different crystalline-field schemes: Curve 1 (for $CeAl_2$) corresponds to a cubic field with a Γ_7 ground state and a splitting $\Delta=100$ K; curve 2 (for $CeCu_2Si_2$) corresponds to three doublets at energies 0, 140, and 360 K. The effective mass is equal to $m=2.72$ for $CeAl_2$ and $m=3.32$ for $CeCu_2Si_2$.

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[17] There is an error in formula (105) of Ref. 2 where the last term $\alpha_i\alpha_l$ must be changed to $\alpha_i\alpha_l(1-1/\lambda_n^2)$. It results that (λ_n^2-1) must be changed to λ_n^2 in formula (110) and (α_1^2-1) to α_1^2 in formulas (114) and (115) of Ref. 2. However, this minor error does not modify the different results of the resistivity calculation presented in Ref. 2.
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