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SEEBECK COEFFICIENT OF CePd₃

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Rare earth compounds have potential applications in thermoelectric devices due to their large value of conductivity and Seebeck coefficient. CePd₃ has the highest reported Seebeck coefficient ($S \sim 125 \mu\text{V/K}$), when doped appropriately, among all rare-earth compounds. This high value is explained as a result of the placement of the cerium f^1 level.

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Most metals have a small Seebeck coefficient and are unsuitable for thermoelectric devices [1, 2]. The exceptions are metals with a localized magnetic moment, such as provided by a rare-earth ion [3, 4]. There are many metallic compounds which contain either cerium or ytterbium which attain Seebeck coefficients in the range of 50–100 $\mu\text{V/K}$ [2, 4]. The highest reported value ($S \sim 125 \mu\text{V/K}$) is found in CePd₃ [3, 5]. Here we wish to explain the reason behind this larger value. Although the difference between 100 and 125 seems small, the larger value represents a breakthrough. The value of 100 $\mu\text{V/K}$ appeared to be a universal maximum [6–9], so that 125 represents an achievement. A value of only 160 $\mu\text{V/K}$ would make a material useful in thermoelectric devices [2].

The efficiency of a thermoelectric device is an increasing function of the dimensionless *figure of merit*

$$ZT = \frac{\sigma TS^2}{K_p + K_e}, \quad (1)$$

$$K_e = \frac{\pi^2}{3} \sigma T \left(\frac{k_B}{e} \right)^2, \quad (2)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, k_B is Boltzmann's constant, and the thermal conductivity is due to phonons (K_p) and electrons (K_e). The latter is proportional to the electrical conductivity according to the Wiedemann–Franz law. The combination of these two relations shows that

$$ZT \leq \frac{\sigma TS^2}{K_e} = \left(\frac{S}{S_0} \right)^2, \quad (3)$$

$$S_0 = \frac{\pi}{\sqrt{3}} \left(\frac{k_B}{e} \right) \approx 156 \mu\text{V/K}. \quad (4)$$

A Seebeck coefficient of over 156 $\mu\text{V/K}$ is needed to get ZT larger than unity, which is needed for efficient device operations.

There have been several reports on the Seebeck coefficient of CePd_3 which ranges in value at room temperature from 80–125 $\mu\text{V/K}$. This material has several bands crossing at the Fermi surface, and the Fermi surfaces are small. Its Seebeck is unusually sensitive to doping. However, the high value of 125 $\mu\text{V/K}$ has been reproduced [10, 11]. The question is why this value is higher than the one of any other metal. The clue was suggested in Ref. [12]. Theoretical calculations by these authors showed that if the energy of a single f -level was made slightly positive with respect to the chemical potential, they obtained a larger Seebeck coefficient. All our calculations, and usually those of others, are based on the single-site Anderson model [13]

$$H = H_0 + V, \quad (5)$$

$$H_0 = \sum_{k\nu} \varepsilon_k C_{k\nu}^\dagger C_{k\nu} + \varepsilon_f \sum_{\mu} n_{\mu} + U \sum_{\mu > \nu} n_{\mu} n_{\nu}, \quad (6)$$

$$n_{\mu} = f_{\mu}^\dagger f_{\mu}, \quad (7)$$

$$V = \frac{1}{\sqrt{N}} \sum_{k\nu} V_{k\nu} \left[f_{\nu}^\dagger C_{k\nu} + C_{k\nu}^\dagger f_{\nu} \right]. \quad (8)$$

The Hamiltonian H_0 has eigenvalues $E_n = n[\varepsilon_f + U(n-1)/2]$, where n is the number of electrons in the f -orbital. The maximum number is $N_f = 14$. The spin-orbit splitting divides the fourteen-fold degenerate state into six and eight states. For cerium, the ground state is in the subband with $N_f = 6$ as the maximum number of available states. The spin-orbit splitting is large, so that the subband with eight states is out of the picture.

Usually one takes $U > 0$, $\varepsilon_f < 0$ so that the ground state has $n \geq 1$. It is this case which has a Seebeck with a maximum of $S = 100 \mu\text{V/K}$ [6, 7, 14]. In these cases, a graph of the Seebeck vs. temperature showed that the Seebeck reached a maximum near to the Kondo temperature, and decreased at higher temperature. The case with $\varepsilon_f > 0$ was calculated in Ref. [12]. They found that the Seebeck increased with temperature without saturation, and there was no maximum. They used the method of renormalization group.

Here we present calculations of the Kondo resonance and Seebeck coefficient using the non-crossing approximation [6, 7, 14]. We took $N_f = 6$, $\varepsilon_f = 0.1 \text{ eV}$, and $U = 6.0 \text{ eV}$. Several values were taken for the hybridization width $\Delta = \pi N + F(V_k^2)$, where N_F is the density of states. We used a Lorentzian density of states with a band width of $D = 1.0 \text{ eV}$. The results are shown in Fig. 1 for a wide range of temperatures. In each case the Seebeck reaches a maximum value and then decreases with increasing temperature. The maximum values depend upon the choice of Δ , but range from 100 to 140 $\mu\text{V/K}$. Our results agree with Ref. [12]

in that we find the values greater than $100 \mu\text{V}/\text{K}$, but disagree in that we always find a maximum in the Seebeck. Thus we have shown that the single site Anderson model can produce values of the Seebeck coefficient large enough to explain the data in CePd₃. This explanation for the data requires that ε_f be a small positive number. Whether this choice is reasonable is discussed below.

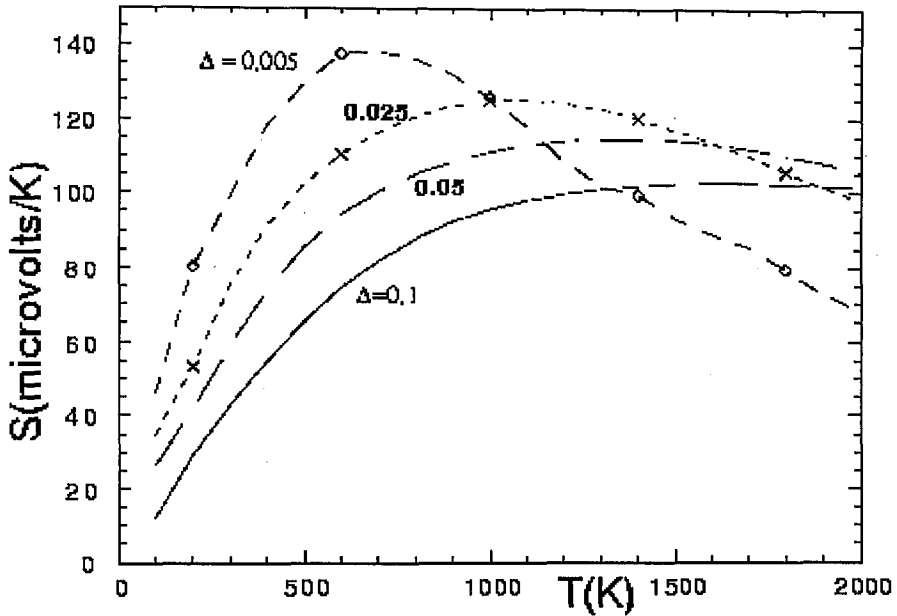


Fig. 1. Seebeck coefficient as a function of temperature as calculated from the Anderson model using the non-crossing approximation. Input parameters used are: $N_f = 6$, $U = 6.0 \text{ eV}$, and $\varepsilon_f = 0.1 \text{ eV}$.

The data in Ref. [3] has the maximum value of the Seebeck at a temperature $T_M = 150 \text{ K}$. What value of Δ does this require? We took the results from Fig. 1 and tried different methods of scaling when graphing T_M vs. Δ . The one that works well is

$$T_M = C\Delta^\alpha, \quad (9)$$

where the empirical values are $C = 3188 \text{ K}$, $\alpha = 2/7$. Using this scaling, a value of $T_M = 150 \text{ K}$ requires the very small value of $\Delta = 23 \mu\text{eV}$. This value seems unphysically small.

The last issue is whether the cerium f^1 energy level in CePd₃ is actually around $\varepsilon_f \sim 0.1 \text{ eV}$. This issue is controversial. Two different types of investigations give conflicting results. Allen and coworkers [15] have measured the density of occupied f -states in many cerium compounds. They isolate the f -levels from the d -bands and other states by utilizing resonances in the photoemission cross sections. In CePd₃ they show a large band of f -states centered about 2.0 eV below the chemical potential. If their results are correct, then $\varepsilon_f = -2 \text{ eV}$, and our hypothesis of $\varepsilon_f > 0$ is incorrect. The argument against the Allen interpretation

is that a lot of processing of the data takes place to obtain their final curves. One cannot measure an f -electron directly in photoemission, since its angular momentum state is too high to convert directly to an s - or p -electron which exits from the solid.

Furthermore, other measurements [5] suggest a cerium valence of around 3.5, which suggests that the f^1 and f^0 levels are similar in energy. Sales [16] analyzed magnetic and transport data, and concluded that the f^1 level was slightly higher in energy than the chemical potential. This placement is where we also put this level. So our work supports the suggestion of Sales.

On the other hand, several different energy band calculations [17–19] all agree that $\varepsilon_f > 0$ and has a small value around 0.1–0.2 eV. We have also done the same calculation using WIEN97 [20] and found the results identical with the ones of earlier workers. Our results are shown in Fig. 2. The f -state is a very flat band right above the chemical potential, which produces a spike-like peak in the density of states. The states about 2.0 eV below the chemical potential are d -like. These calculations all support the present interpretation. The argument against the band structure calculations is that they are notorious for misplacing the location of the f -levels. We believe that this problem is not applicable when the f -levels are unoccupied, as they are in the present case. Nonetheless, the placement of f -levels, in band structure calculations, is always tricky.

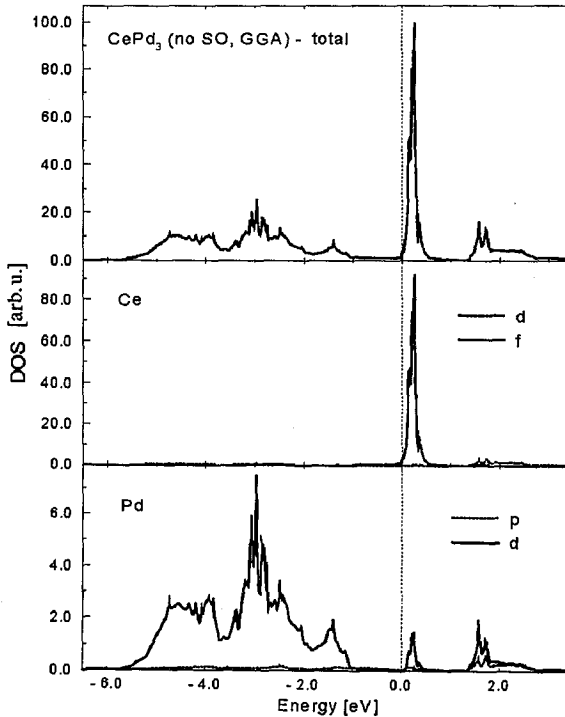


Fig. 2. Calculated density of states of CePd_3 . The sharp, narrow, peak above the chemical potential is due to the empty state f^1 .

The issue of where the f -electron levels are located is sometimes controversial. One notable example is in YbAl₃ where several groups heatedly disagreed whether the f -level was near to the chemical potential or well below it [21–26]. CeRu₂ and CeIr₂ are two examples where photoemission does place the f^1 level near to the chemical potential [27].

In conclusion, we suggest that the high value of the Seebeck coefficient in CePd₃ is due to having the f -level unoccupied and slightly higher in energy than chemical potential. Of course, it is then partially occupied by the valence fluctuations between the $n = 0$ and $n = 1$ configurations. These fluctuations give the large value of the Seebeck. They are not found when ε_f is a small negative number, but only in the case of a small positive number. This assignment agrees with several energy band calculations, and with transport data, but disagrees with resonant photoemission. Further work is needed to test the correctness of this hypothesis.

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