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Thermopower of (Ce, Pr)Cu₆ alloys†

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Abstract. We report on the thermopower of (Ce_x, Pr_{1-x})Cu₆ for $0 \leq x \leq 1$ from 2 K up to room temperature. Over the studied temperature range, it is found that the thermopower is positive and show a maximum except for pure PrCu₆. Besides the maximum, we notice a shoulder at low temperature. With increasing Pr concentrations, the shoulder becomes more apparent and almost comparable in size to the main maximum. Using the Nordheim–Gorter rule, we have been able to estimate the magnetic contribution of Ce to the thermopower, which is found to be $50 \mu\text{V K}^{-1}$ at the maximum. We also report the thermopower of PrCu₆ for the first time. It is positive over the studied temperature range. PrCu₆ also shows a modest maximum at higher temperature. This maximum, however, is much broader and smaller than that for the Ce-rich side of CeCu₆.

1. Introduction

Among several earlier heavy-fermion compounds, up to now it has been found that CeCu₆ alone remains non-magnetic. Although it is rather surprising to have magnetic ground states in heavy-fermion compounds with such small ordered moments of the order of $0.01 \mu_B$, it is also nearer to the truth to say that there is no clear-cut understanding of how one system become non-magnetic but another does not. Qualitative arguments have been provided by Doniach [1]; his one-dimensional Kondo necklace model explains the magnetic instability using competition between two energy scales, i.e. a single-site Kondo screening (T_K) and an intersite magnetic Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction (T_{RKKY}). It thus looks especially interesting to us to study thoroughly the non-magnetic ground state of CeCu₆.

In this context, one may recall that among earlier non-magnetic heavy-fermion compounds CeRu₂Si₂ is now known to have somewhat static ordered moment with improving sample qualities and perhaps more careful studies [2]. For CeCu₆, however, down to the lowest measured temperature, only short-range antiferromagnetic fluctuations have been observed by neutron scattering [3] and a metamagnetic transition has been seen around 2 T [4].

Apart from the non-magnetic ground state, CeCu₆ exposes an interesting aspect of concentrated Kondo compounds, or Kondo lattices as they are often dubbed. In most

† This work was initiated when two of us (J-G Park and S B Roy) were with Professor B R Coles at Imperial College, London.

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transport measurements, CeCu₆ shows a coherence-related feature at low temperatures; for example, it has an abrupt drop in resistivity below around 16 K. About the coherence, it is to be noted that, as far as we can see, this is only a difference between dilute and concentrated Kondo systems. In the CeCu₆ case, this coherence in resistivity is known to be relatively more susceptible to a Cu-site doping than a Ce-site doping. From the previous study by one of authors [5], it is shown that in (Ce, Pr)Cu₆ alloys this coherence only disappears by substituting Ce with more than 15% Pr; in the case of Cu-site doping with Al or Au, this value is as small as 2 to 5%.

For studying (Ce, Pr)Cu₆, we think that a thermopower technique is interesting and, to some extent, unique compared with other thermodynamic measurements, because thermopower reflects the energy derivative of the density of states at the Fermi level.

A common feature in the thermopower of Ce-based heavy-fermion compounds is that there is almost always a large and broad maximum, whether the system is concentrated or dilute. Even in Ce mixed-valence systems, such a peak has been observed. It is interesting though that an amorphous CeCu₆ does not show any indication of such a maximum [6], although as far as thermodynamic properties, such as specific heat and susceptibility measurements, are concerned, one can hardly tell an amorphous CeCu₆ from a crystalline CeCu₆.

Admitting our limited understanding of the maximum in thermopower, we would like to mention some theoretical studies. Using the Coqblin–Schrieffer Hamiltonian, Bhattacharjee and Coqblin [7] show that the temperature of the maximum T_M in thermopower is related to the overall crystal-field splitting Δ_{CF} . T_M appears in between $\Delta_{CF}/6$ and $\Delta_{CF}/3$ in two-level systems, but including higher crystal level does not change the position of the maximum in thermopower very much.

Concerning the concentration dependence of the peak, there are somewhat confusing reports. Although the maximum temperature T_M is seen to decrease with increase in La concentrations in (Ce, La)Al₃ [8, 9] and (Ce, La)In₃ [10], it is concentration independent in (Ce, La)Cu₆ [11]; La doping in Ce compounds acts as a source of negative chemical pressure by increasing lattice constants. Since Pr doping is known to decrease the lattice constants of CeCu₆, our studies, we think, can also bring some light on the problem of the concentration dependence of the maximum in thermopower.

2. Experiment

The preparation of the alloys is as described elsewhere [5]. In fact, we made use of the samples of (Ce_x, Pr_{1-x})Cu₆, $x = 1, 0.95, 0.5,$ and $0.25,$ used for the previous studies. However samples with $x = 0, 0.007,$ and $0.07,$ have been manufactured for this study. To make samples with $x = 0.007$ and $0.07,$ we first prepared two parent compounds and then melted them in appropriate proportions to these compositions. Although in principle our samples are polycrystalline, our data suggest that they may have the *ab* plane of the orthorhombic CeCu₆ structure aligned more along the sample rod. This conjecture is supported by magnetic anisotropy measurements [12].

The dimensions of the samples were about $10 \times 1.5 \times 1.5$ mm³. We have measured thermopowers using a differential method. Temperature gradient across the samples was kept at $\Delta_T = 0.25$ K ($\pm 4\%$) from 2 to 20 K, $\Delta_T = T/100$ K ($\pm 10\%$) from 20 to 100 K and $\Delta_T = 1$ K ($\pm 10\%$) from 100 to 300 K. Voltage connections were made through copper wires (30 μ m in diameter) fixed on the sample by silver paint. Contact resistance was not more than 1.5 Ω . The thermopower of the copper connection wires was measured in situ against a high- T_c compound YBaCuO ($T_c = 82$ K) up to 70 K and, at higher temperatures,

against pure lead. For higher temperature measurements, we used the thermopower of lead measured by Roberts [13] to determine the absolute thermopower values of our copper wires. The temperature difference was measured by AuFeO.07%–chromel thermocouples (80 μm in diameter), which are sensitive at low temperatures. In some cases, chromel–constantan thermocouples were used in order to check the thermopower at intermediate and higher temperatures. The thermocouples were glued on the sample by GE varnish. To ensure electrical isolation and an equal distance between the sample and the thermocouples, we put a piece of cigarette paper soaked in GE varnish in between the ends of the sample and the thermocouples. We also glued the thermocouple leads as well as voltage connections around a post to ensure no temperature gradient on either end of the samples.

The thermopowers as well as the thermocouple voltages were measured by two Keithley nanovoltmeters. The process of establishing the temperature difference between the ends of the samples was monitored by a personal computer.

3. Results and analysis

We present the thermopower data of (Ce, Pr)Cu₆ alloys in figure 1, from 2 K up to room temperatures. As one can see, the thermopower is positive over the temperature range for all concentration ranges. One can also notice that for all concentration ranges except for pure PrCu₆ our thermopower data show a large maximum below 100 K. In fact, our CeCu₆ data have a maximum at 50 K in agreement with the reported data [14] but slightly higher than the maximum temperature for a single-crystal CeCu₆ [11]. It is interesting to note that even in a dilute case the thermopower is relatively large. However, changes are noticed to be moderate from a Ce-dilute sample to a Ce-rich sample. For example, although the Ce concentration is 143 times larger in CeCu₆ than in 0.7% Ce-doped PrCu₆, the maximum mentioned above is merely 4.5 times bigger in CeCu₆. Since this maximum appears progressively with doping Ce, we think electron scattering from Ce atoms is responsible for it.

It is further noteworthy that the thermopower has a shoulder around 6 K for $x = 1$ and $x = 0.95$. With further Pr doping, this shoulder becomes more clear and almost comparable to the main maximum in the most Ce-dilute sample, 0.7% Ce-doped PrCu₆. As to the origin of such a low-temperature maximum, there are two scenarios: one due to an ordinary Kondo effect [15] and another due to a spin fluctuation temperature [16]. As we mentioned in the previous section, the appearance of this shoulder in our measurements indicates that our polycrystalline samples have the *ab* plane of orthorhombic CeCu₆ structure aligned more along the sample direction [17]; remember our sample is in a rod shape. It is also interesting to note that thermopower shows small humps around 200 K on the background of the dominant maximum for CeCu₆ and (Ce_{0.95}Pr_{0.05})Cu₆ and the hump seems to move towards higher temperature with Pr doping before disappearing in (Ce_{0.5}Pr_{0.5})Cu₆. It may well be due to a structural transformation seen in CeCu₆ [18].

To get magnetic contributions to the thermopower, we used the Nordheim–Gorter rule [9]:

$$S_{\text{mag}} = (1/\rho_{\text{mag}})(S_{\text{M}}\rho_{\text{M}} - S_{\text{lattice}}\rho_{\text{lattice}})$$

where S_{mag} and ρ_{mag} represent contributions to thermopower and resistivity from scattering by Ce 4f electrons. S_{M} and ρ_{M} denote measured thermopower and resistivity at temperature. S_{lattice} and ρ_{lattice} represent other contributions, such as phonon, to thermopower and to resistivity. We estimated these phonon contributions using our experimental data for PrCu₆. Although we have also used non-magnetic LaCu₆ as a reference material during our study, we feel that PrCu₆ is as good a reference as LaCu₆, and perhaps a little bit better. This may

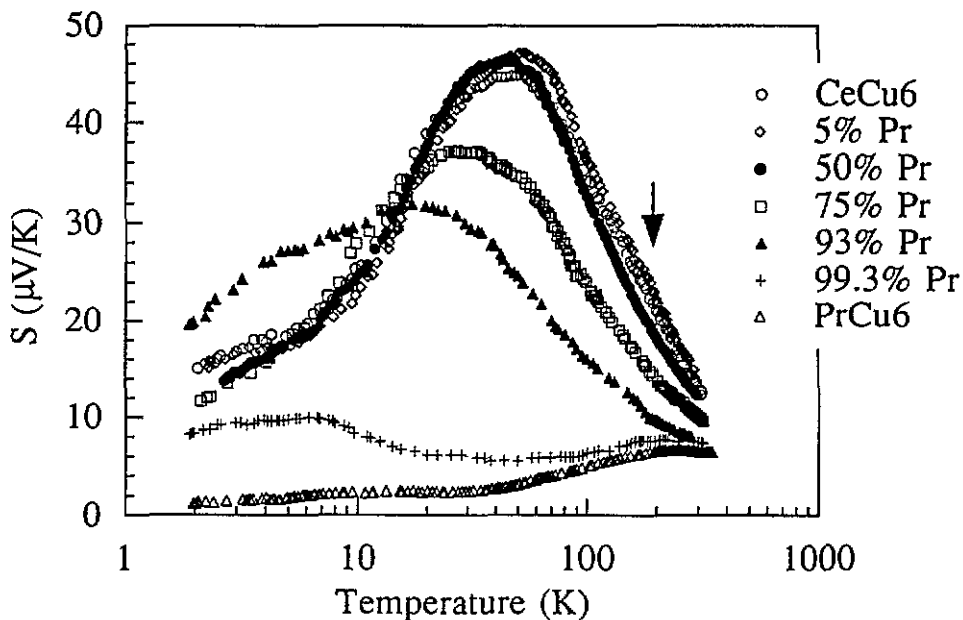


Figure 1. Thermopower measurements of $(\text{Ce}_x, \text{Pr}_{1-x})\text{Cu}_6$ alloy system. The arrow indicates where small humps appear for $x = 1$ and 0.95 (see the text).

be because we then subtract from the total thermopower any contribution from Pr scattering with a clearer indication of the Ce scattering effects. In fact, the magnetic scattering from Pr atom is more evident at temperatures higher than 100 K, which also coincides with a structural transformation around 200 K (see figure 1); PrCu_6 changes from an orthorhombic CeCu_6 type to monoclinic at that temperature [19]. However, we have to admit that some complications are to be expected as alloys become Ce-rich.

Table 1. Physical quantities evaluated from the resistivity and the thermopower measurements for $(\text{Ce}_x, \text{Pr}_{1-x})\text{Cu}_6$ (see the text for an explanation of the symbols).

x	T_M (K)	S_M ($\mu\text{V K}^{-1}$)	ρ_M ($\mu\Omega \text{ cm}$)	ρ_{lattice} ($\mu\Omega \text{ cm}$)	S_{lattice} ($\mu\text{V K}^{-1}$)	$S_{\text{mag}}(T_M)$ ($\mu\text{V K}^{-1}$)	$x^{1/2}/T_M$ (K^{-1})
0.007	6	10	3.5	3	2.5	55	0.014
0.07	15	32	13.5	3.5	2.5	42.3	0.018
0.25	25	37	34	6	2.5	44.4	0.02
0.5	40	46	56	8	2.7	53.6	0.017
0.95	50	47	70	11.5	2.9	55.7	0.019
1	50	44.5	64	11.5	2.9	53.6	0.02

In table 1, we summarize results from the analysis using the Nordheim–Gorter rule: T_M ; temperature where thermopower has a maximum; S_M ; thermopower at T_M ; ρ_M ; resistivity of the alloys at T_M ; ρ_{lattice} resistivity of PrCu_6 at T_M , from [5]; and S_{lattice} thermopower of PrCu_6 at T_M . The resistivity value for $x = 0.07$ was estimated from a linear interpolation between the values for $x = 0.1$ and $x = 0.007$. We also present our estimations of $S_{\text{mag}}(T_M)$, the magnetic contribution to the thermopower at T_M .

Considering our estimates of $S_{\text{mag}}(T_M)$, one can reach the same conclusion as that drawn

by Cibir *et al* [9] that the magnetic contribution is independent of Ce concentration; the values are rather uncertain for the lowest concentration, i.e. $x = 0.007$. The same conclusion can also be made when LaCu₆ is used as a reference material instead of PrCu₆, except for a small decrease in our $S_{\text{mag}}(T_M)$ for the LaCu₆ case.

Although the magnetic contributions, $S_{\text{mag}}(T_M)$, are independent of Ce concentration, the temperatures of the peak, T_M , are found to increase with Ce concentrations. Indeed T_M is roughly proportional to the square root of the Ce concentration (see table 1). When we plot S_{mag} as a function of temperature, however there is no Ce concentration dependence of T_M in S_{mag} (see figure 2). So magnetic thermopower S_{mag} has both T_M and $S_{\text{mag}}(T_M)$ independent of Ce concentrations. Since it is more appropriate to use magnetic thermopower rather than total thermopower for the purpose of discussing effects by Ce 4f electrons, we concentrate our discussions on magnetic thermopower data of (Ce, Pr)Cu₆. The concentration-independent T_M behaviour seems to be at odds with a lattice-pressure argument [8], which is often used when one tries to explain the concentration dependence of the crystal-field splitting parameter Δ_{CF} . If we follow the same argument, T_M is expected to decrease with Ce concentrations because of a volume expansion due to Ce doping. Regarding this puzzling T_M behaviour with Ce doping, it may be interesting to note that in previous Ce(Cu, Au)₆ studies [14] T_M was seen to increase with Au doping, although since concentrations of Au increase the lattice constants one would then expect a decrease in Δ_{CF} . Therefore the trend of T_M seen in Au-doped CeCu₆ is not explainable by a simple lattice-pressure argument either. In fact, later neutron studies confirm that crystal-field splittings between the three doublets become bigger with Au doping. Incidentally T_M in La doped CeCu₆ is almost concentration independent [11]. Bearing in mind that most conclusions drawn on the above systems are based on total thermopower data, not like ours using magnetic contributions, two possibilities are emerging as to the concentration dependence of T_M and $S_{\text{mag}}(T_M)$. (i) The crystal-field splitting might not change with Pr doping on the Ce site of CeCu₆ despite the decrease in volume by Pr doping. When all Ce are replaced by Pr, volume is expected to decrease by 0.7%. For comparison, the lowest inelastic transition in neutron data [20] increases from 7 meV for CeCu₆ to 8 meV for CeCu_{5.5}Au_{0.5}, whereas hybridization is expected to decrease as volume increases by 1.4% [13]. (ii) The lattice-pressure argument is not simply adequate enough, so perhaps we may need to consider effects due to another characteristic energy scale such as Kondo temperature as discussed by Hanzawa *et al* [21].

In figure 2, we plot magnetic thermopower of (Ce, Pr)Cu₆. It is noticeable that most data fall on top of one another with similar T_M and $S_{\text{mag}}(T_M)$ values. To analyse the thermopower data, we used the same formula as in [22]. Although it was originally developed for intermediate-valence compounds, surprisingly enough the formula appears to be able to describe well our data across the whole range of concentration except for PrCu₆. Having said that, we do not attempt to go into much detail of the analysis since it was developed for charge, not spin, fluctuation systems. The line under the data is given by fitting the results using the formula

$$S(T) = AT/(B^2 + T^2)$$

with

$$A = 2(\epsilon_f - \epsilon_F)/|e| \quad B^2 = 3[(\epsilon_f - \epsilon_F)^2 + \Gamma^2]/(\pi k_B)^2$$

where subscript f relates to 4f electrons and F to Fermi level. The two parameters A and B are related to the Lorentzian that extends across the Fermi level. In our analysis, we found that $A = 7600 \mu\text{V}$ and $B = 65 \text{ K}$ give the best fit, which give $\epsilon_f - \epsilon_F = 3.8 \text{ meV}$,

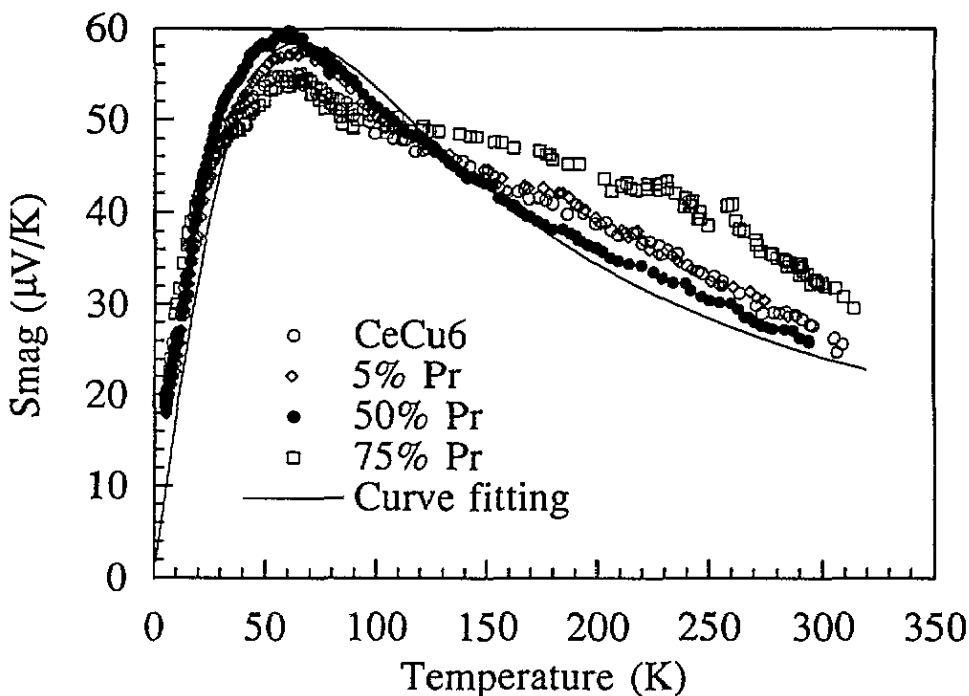


Figure 2. Magnetic thermopower data and curve fitting results for $(\text{Ce}_x, \text{Pr}_{1-x})\text{Cu}_6$ (see the text).

$\Gamma = 9.5$ meV, the valence of Ce ion $\nu = 3.21$ and estimated electronic specific heat $\gamma = 143$ mJ mol⁻¹ K⁻². Compared with values for typical mixed-valence compounds (for example, CeSn₃ has $\epsilon_f - \epsilon_F = 6$ meV and $\Gamma = 30.7$ meV [22]), curve-fitting results seem to be consistent with the fact that many-body resonance is nearer the Fermi level and narrower in spin fluctuating systems such as CeCu₆ than in charge fluctuating systems. However, there is a clear disparity between values given here and values directly estimated from other experiments. Quasielastic neutron data reveal $\Gamma = 1$ meV and specific heat measurements show $C/T = 1600$ mJ mol⁻¹ K⁻².

Regarding the data for PrCu₆, it is interesting to note that we have a broad maximum at low temperatures (around 10 to 20 K) where the first excited state lies [19] and the specific heat shows a hump due to crystal-field splitting [5]. Another maximum appears at much higher temperature where a structural transformation is reported to occur [19]; this maximum is also seen in a 0.7% Ce-doped sample. As Ce concentrations increase, however, the more dominant feature is the magnetic contribution from Ce ions.

4. Discussion

Compared with published thermopower results on La- and Au-doped CeCu₆ [11, 14], the following features are to be noted. First of all, we note that Pr-doped CeCu₆ has a positive thermopower over the experimental temperature range like La-doped CeCu₆. This behaviour is different from what is seen in Au-doped CeCu₆, where there appears a negative maximum at low temperatures with 20% Au doping, which was interpreted as a sign of incipient magnetic order [14]. If that interpretation is correct, both Pr and La doping would seem to

depress intersite antiferromagnetic interactions, although Pr doping reduces lattice constants while La doping does otherwise. The onset of antiferromagnetism in Ce(Cu, Au)₆ has been ascribed to a reduction of hybridization by lattice expansion. Secondly, we note that the thermopower has a large maximum in the La- and Pr-doped CeCu₆ samples even in dilute Ce compounds such as 7% Ce doped PrCu₆. This is a little surprising and contrasts with the behaviour of Au-doped CeCu₆, where the maximum in a 20% Au-doped sample has already become half that of pure CeCu₆, although all La-doped CeCu₆ samples have a larger maximum than pure CeCu₆. Perhaps the great difference in the effects of doping on the ligand sites and the Ce sites seen in ρ may mean that lattice expansions by doping on the different sites may not produce equivalent effects on magnetic interactions or the thermopower maximum. Our results thus support the indications from resistivity that Ce-site doping differs significantly from Cu-site doping regardless of the doping material. Finally, the low-temperature shoulder becomes more marked and moves toward lower temperatures with Pr doping, a feature also seen in the La-doped CeCu₆.

Why does the formula originally developed for charge fluctuating systems work here? We think that it may be due to the Lorentzian low-lying excitations required by the theory [22]. And a Lorentzian form may not be a bad approximation for the excitation spectrum of spin fluctuation systems as well as charge fluctuation systems. That there is a strong similarity in thermopower data for both mixed valence and heavy-fermion systems may not be irrelevant in this respect. As is clearly shown in our case, however, any analysis using this formula cannot go beyond qualitative estimations.

Concerning the behaviour of T_M , at which a maximum in thermopower occurs, its contrasting behaviour in such systems as (Ce, La)Cu₆ [11], (Ce, Pr)Cu₆, (Ce, La)In₃ [10] and (Ce, La)Al₃ [8, 9] indicates that it is influenced by both the system and the specific doping material, since an appreciable concentration dependence is found in the last two systems.

In conclusion, the thermopower of the (Ce, Pr)Cu₆ for all Ce concentrations is positive over the studied temperature range. Except for PrCu₆, we have observed a large maximum below 100 K. Concerning the concentration dependence of the peak, we cannot at the moment give an explanation why such a dependence is seen in some systems but not in others. However, it is advisable to get magnetic thermopower data of systems for proper analysis.

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