

1 Thermoelectric power in CeT_4M ($T = Cu, Ni$; $M = In,$
2 Ga) compounds

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7 **Abstract**

CeCu₄In and CeCu₄Ga compounds belong to heavy fermion (HF) systems. CeNi₄In and CeNi₄Ga seems to be on the border between HF and mixed-valence (MV) states. It has been observed that thermoelectric power (TEP) shows a significant difference between these Cu and Ni-based compounds, whereas thermal conductivity does not reveal such dramatic changes in the temperature dependencies. These results are analyzed assuming the Kondo effect at presence of the crystal electric field for the HF compounds and two density of states peaks in the region of the Fermi level for the remaining compounds. The details of the electronic structure are supposed to be responsible for the negative TEP of CeNi₄M.

8 *Key words:* A. intermetallics, C. heavy fermions, C. electrical transport,
9 C. heat capacity, kondo effect, C. thermoelectric, C. valence fluctuations
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11 **1. Introduction**

12 The heavy fermion (HF) state in CeCu₄M compounds has already been
13 confirmed for $M = Al$ and Ga [1, 2, 3, 4, 5] from the investigation of the
14 magnetic, transport and thermodynamic properties. CeCu₄Ga was found to
15 be nonmagnetic down to 30 mK, whereas the parent Kondo lattice compound
16 CeCu₅ is antiferromagnetic below 4 K. Similar drop of the magnetic order
17 occurs for CeCu₄Al [1, 2, 3, 4, 5, 6] and CeCu₄In [7]. The electronic specific
18 heat coefficient of CeCu₄M takes huge values of the order of 2-3 JK⁻²mol⁻¹.
19 The electrical resistivity studies have shown that the Kondo temperature is
20 in the range 2-5 K and below about 1 K the coherence onset occurs [1, 2, 3,

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21 4, 5, 6, 7, 8]. A large peak in thermopower (TEP) was observed for CeCu₄Ga
22 [5] at temperature much higher than the Kondo temperature.

23 CeNi₄M compounds reveal features typical of mixed-valence (MV) sys-
24 tems. We have observed the MV state for M = Al, B, Cu, Cr, In and Ga
25 [7, 9, 10, 11, 12, 13, 14], with a tendency to HF state in the case of M = Cu
26 and Cr [11, 12]. CeNi₄In and CeNi₄Ga, which also seem to be on the border
27 between HF and MV state will be further denoted shortly by MV.

28 The studies of TEP carried out by Koterlyn *et al.* [15] for CeNi₄In have
29 revealed negative thermopower in the whole temperature range studied. This
30 compound was suggested to be in the saturated valence (SV) state.

31 In the present paper we compare the thermoelectric properties of the
32 HV CeCu₄In and CeCu₄Ga compounds with the MV CeNi₄In and CeNi₄Ga
33 compounds, including the effect of the crystal electric field (CEF) for the HF
34 systems.

35 2. Experimental details

36 The polycrystalline CeCu₄M and CeNi₄M compounds have been pre-
37 pared by the induction melting under an argon atmosphere. As the ingot in
38 the water cooled crucible the stoichiometric amounts of the pure elements
39 were used.

40 The crystal structure was checked and confirmed by the powder X-ray
41 diffraction technique, using the Co-K_α radiation. We have observed that
42 CeCu₄In crystallizes in the orthorhombic structure of the CeCu_{4.38}In_{1.62}-
43 type within the space group *Pnmm* [16, 17]. The lattice constants are $a =$
44 16.675 \AA , $b = 10.589 \text{ \AA}$ and $c = 5.046 \text{ \AA}$. This structure is obtained from
45 CeCu₆ by mutual change of the b and c parameters and putting $2a$ instead of
46 the a parameter. CeCu₄Ga crystallizes in the hexagonal CaCu₅-type struc-
47 ture, space group *P6/mmm*. The structure of all the CeNi₄M compounds we
48 have studied till now is hexagonal of the CaCu₅-type, apart from CeNi₄B be-
49 ing hexagonal of the CeCo₄B-type and CeNi₄In being cubic of the MgSnCu₄-
50 type (space group *F43m*, $a = 7.062 \text{ \AA}$).

51 The thermoelectric power, electrical resistivity and thermal conductivity
52 were measured using the commercial PPMS device (Quantum Design). Four-
53 probe mode was employed in all the measurements.

54 The samples were in a shape of bars with typical dimensions of about
55 $1 \times 1 \times 8 \text{ mm}^3$.

56 **3. Thermopower**

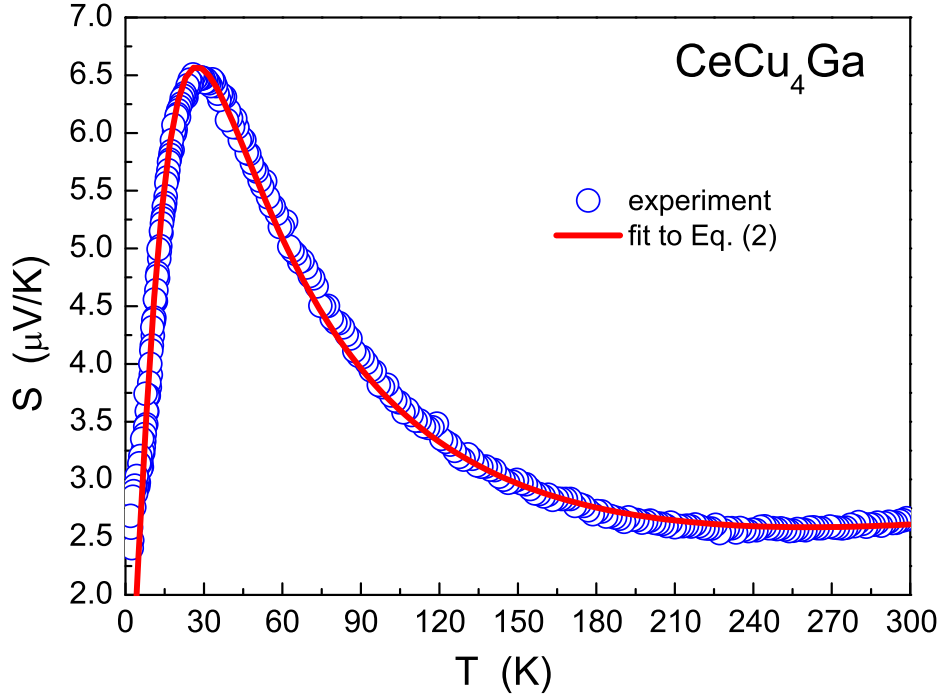


Figure 1: Thermopower of CeCu₄Ga (circles). Solid line: fit according to Eq. (2).

57 In Fig. 1 the temperature dependence of thermopower, $S(T)$, of the
 58 CeCu₄Ga compound is shown together with a calculated curve. One can
 59 see a large maximum of $S(T)$ at 28 K. On the other hand, it is well estab-
 60 lished that the Kondo temperature of this compound is about 1.8-2.4 K [5, 8];
 61 therefore, this TEP peak is mainly due to the competition between CEF and
 62 the Kondo effect.

63 We have carried out an analysis of the measured TEP basing on the model
 64 assuming scattering of electrons from the wide conduction band into a narrow
 65 f-band approximated by a Lorentzian shape [18]. TEP is then expressed by
 66 the formula:

$$S_f(T) = \frac{2 k_B}{3 |e|} \frac{\pi^2 E_f T}{(\pi^2/3)T^2 + E_f^2 + W_f^2}, \quad (1)$$

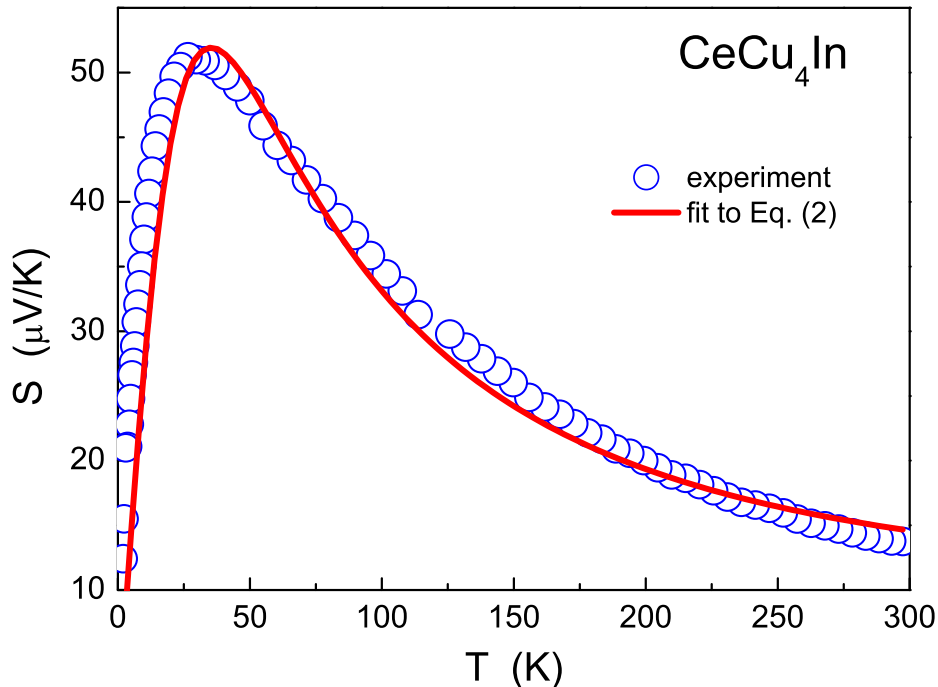


Figure 2: Thermopower of CeCu_4In (circles). Solid line: fit according to Eq. (2).

67 where E_f and W_f are the position and width of the f-band in Kelvins. Eq. (1)
 68 has been satisfactory used for the description of mixed-valence systems, i. e.
 69 systems characterized by large values of T_K . Eq. (1) can be rewritten in the
 70 course of T_K using the relations: $E_f = T_K$, $W_f = \pi T_K / N_f$, where N_f is the
 71 orbital degeneracy $2J+1$. We cannot use these relations and Eq. (1) as we
 72 have the HF system of low Kondo temperature. In our case Eq. (1) describes
 73 rather a scattering of conduction electrons on an ensemble of incoherent im-
 74 purities than on a narrow f-band. Therefore, we make a rough assumption
 75 that in the case of the energy scale dominated by the crystal electric field
 76 the line width in Eq. (1) is determined mainly by T_{CEF} , i. e. we make the re-
 77 laxation time energy dependent. It means that the fastest relaxation process
 78 determines the line width, which is the physically expected case. Hence, the
 79 substitution $W_f = \pi T_{\text{CEF}} / N_f$ is used for $T > T_K$ and finally the formula

$$S(T) = S_f(T) + S_0(T), \quad (2)$$

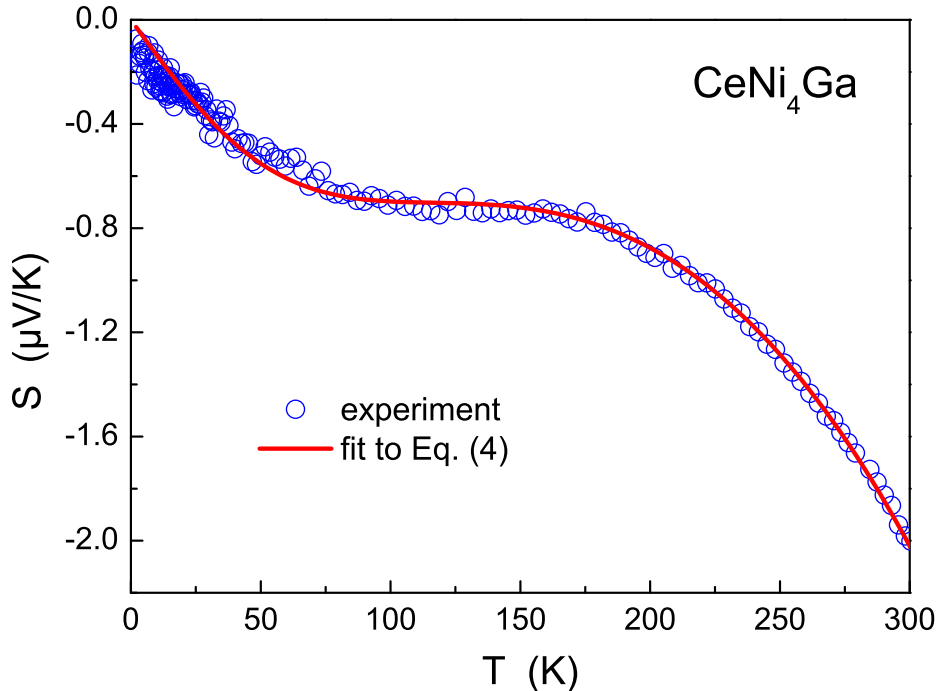


Figure 3: Thermopower of CeNi₄Ga (circles) fitted with Eq. (4) (solid line).

80 was used to obtain the solid line in Fig. 1 and Fig. 2.

81 We do not use the nonmagnetic reference samples in the TEP measure-
 82 ments, therefore, the calculated curves are obtained by adding additional
 83 linear term of the form $S_0(T) = aT$ (Eq. (2)), which accounts for other than
 84 the Kondo and CEF contributions. It is the often employed procedure [19].
 85 The linear parameter a can in general be responsible for several effects but
 86 is mainly due to the nonmagnetic Mott-type scattering [19, 20, 21], which is
 87 determined by the Fermi energy.

88 The importance of the competition between the Kondo and CEF scales
 89 have already been emphasized in Ref. [22, 23]. One could also think about
 90 the Kondo temperature distribution as the source of the TEP peak, however
 91 the width of such a distribution would have to be very large compared with
 92 the small T_K itself.

93 The refinement of the TEP peak for CeCu₄Ga in Fig. 1 with Eq. (2) (solid
 94 line) is obtained for $a = 4.9 \times 10^{-3} \mu\text{V}/\text{K}^2$, $T_K = 2$ K and $T_{\text{CEF}} = 32$ K, 64 K,

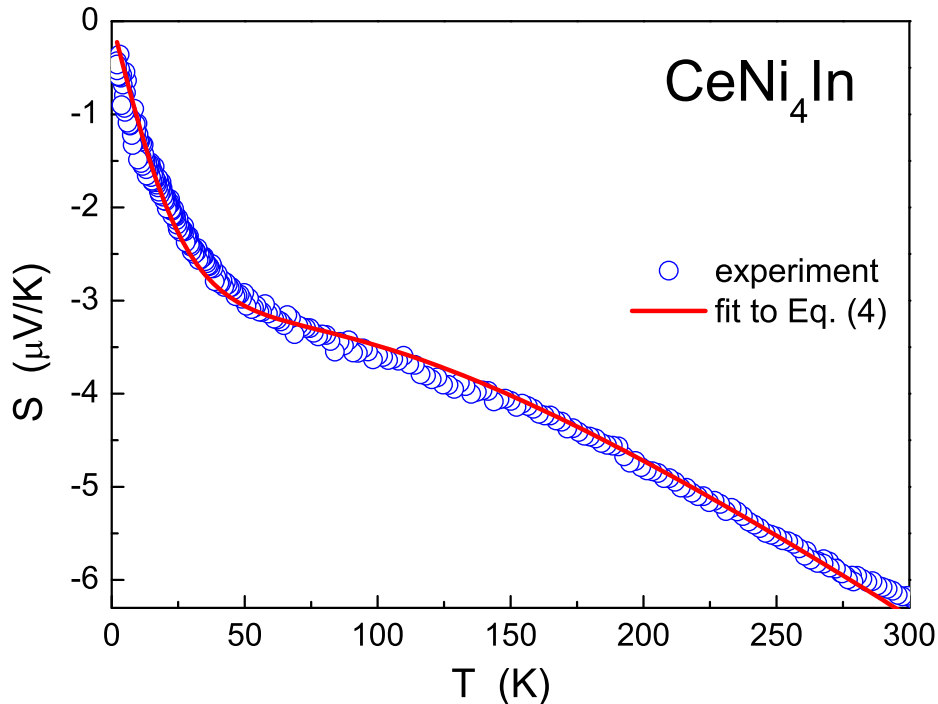


Figure 4: Thermopower of CeNi₄In (circles) fitted with Eq. (4) (solid line).

95 and 96 K provided that the degeneracy $N_f = 2, 4,$ and $6,$ respectively. The
 96 estimation carried out for CeCu₄Ga based on the inelastic neutron scattering
 97 ($\Delta = 70$ K) [3] is in a reasonable agreement with our result assuming the
 98 degeneracy close to $N_f = 4$ in our TEP analysis.

99 Similar analysis has been carried out for the CeCu₄In compound. Eq. (2)
 100 provided $a = 9 \times 10^{-3} \mu\text{V}/\text{K}^2,$ $T_K = 21$ K and $T_{\text{CEF}} = 38$ K, 76 K, and 115 K
 101 for the corresponding degeneracies. The estimation derived from the specific
 102 heat measurements is $\Delta \approx 80$ K. Again, the degeneracy close to $N_f = 4$
 103 assumed in the TEP analysis provides best agreement. It should be empha-
 104 sized that there are no fixed parameters in the TEP analyzes of CeCu₄Ga
 105 and CeCu₄In with Eq. (2). The values of the CEF splitting between 70 - 90 K
 106 for CeCu₄Ga and CeCu₄In are similar to our recent studies on the CeCu₄Al
 107 compound [24], where the possibility of a quasi-quartet state, i. e. CEF levels
 108 scheme of the type $0 - 93$ K has been discussed.

109 Figures 3 and 4 depict the temperature dependence of TEP for the
 110 CeNi₄Ga and CeNi₄In compounds. These compounds have been classified
 111 as MV systems [7, 13]. TEP is negative in the whole temperature range
 112 studied. It can partly result from the electronic structure, i. e. in contrast to
 113 the Cu-based compounds Ni provides partly unfilled 3d states. Since TEP is
 114 proportional to the density of states (DOS)

$$S_d \propto T \left(\frac{d \ln N_d(E)}{dE} \right)_{E_F} \quad (3)$$

115 a negative TEP can be developed for a negative gradient of DOS.

116 In accordance with these hints we make the attempt to fit the $S(T)$
 117 dependence of CeNi₄Ga and CeNi₄In engaging two Lorentzian peaks within
 118 the region of the Fermi level. Hence, the experimental results plotted in
 119 Fig. 3 and 4 are analyzed with the relation

$$S_f(T) = c_1 \cdot \frac{2 k_B}{3 |e|} \frac{\pi^2 E_{f1} T}{(\pi^2/3)T^2 + E_{f1}^2 + W_{f1}^2} + c_2 \cdot \frac{2 k_B}{3 |e|} \frac{\pi^2 E_{f2} T}{(\pi^2/3)T^2 + E_{f2}^2 + W_{f2}^2} + aT, \quad (4)$$

120 which yields $c_1 = 0.052$, $E_{f1} = -1.8$ meV, $W_{f1} = 16.6$ meV and $c_2 = 988$, $E_{f2} =$
 121 1.35 eV, $W_{f2} = 1.6$ eV, $a = -15 \times 10^{-3} \mu\text{V}/\text{K}^2$ for CeNi₄Ga, where c_1 and c_2 are
 122 weights of the Lorentzian contributions. In the case of CeNi₄In the values
 123 are $c_1 = 3.49$, $E_{f1} = -27$ μeV , $W_{f1} = 7$ meV and $c_2 = 862$, $E_{f2} = 1.65$ eV,
 124 $W_{f2} = 4.36$ eV, $a = -3.2 \times 10^{-3} \mu\text{V}/\text{K}^2$. It results from these parameters that
 125 one of the peaks lies nearly at the Fermi level, whereas the second one is
 126 relatively far away from E_F .

127 4. Thermal and electrical conductivity

128 Figure 5 shows the thermal conductivity of the CeCu₄ M and CeNi₄ M
 129 compounds measured as a function of temperature in the range 2-300 K.
 130 One can see that the course of $\lambda(T)$ differs between the Ni and Cu-based
 131 compounds, especially the slope of the linear part is increased for CeCu₄ M .
 132 Knowing the thermal conductivity and the electrical resistivity (the latter
 133 already published in [7, 13]) one can plot the Lorentz number $L(T) =$
 134 $\lambda(T)\rho(T)/T$ normalized to $L_0 = 2.45 \times 10^{-8} \text{ W}\Omega/\text{K}^{-2}$. L/L_0 is plotted vs.
 135 temperature in Fig. 6a and it is visible that the values are strongly increased
 136 for the Ni-based samples.

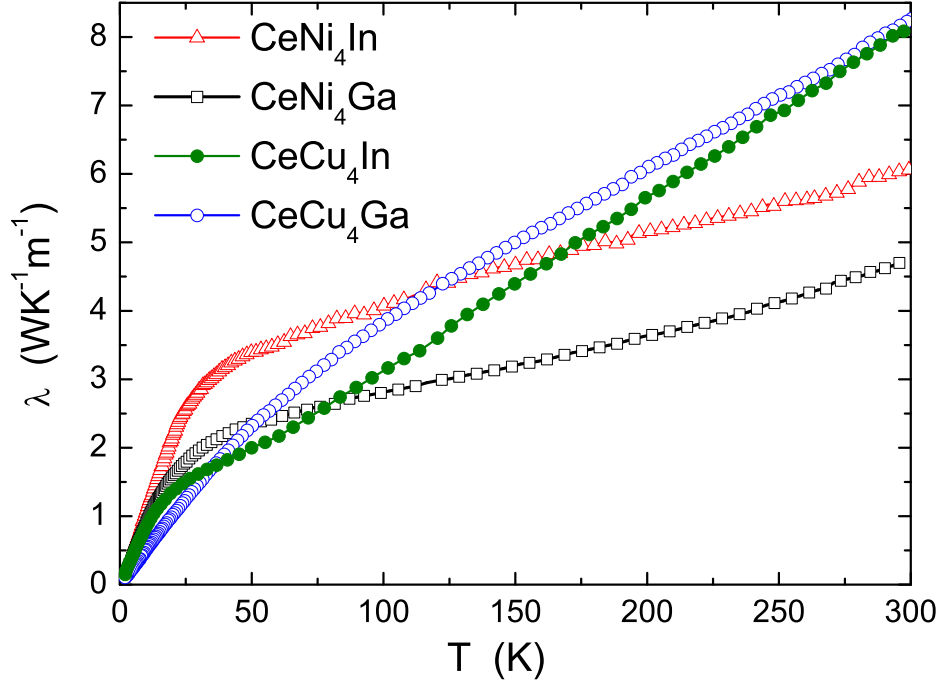


Figure 5: Thermal conductivity of the CeCu_4M and CeNi_4M compounds.

137 According to the Wiedemann-Franz law the ratio L/L_0 should aim at one
138 if the the lattice vibrations can be neglected. Therefore, to display better the
139 relative changes, in Fig. 6b we have re-scaled L/L_0 in such a way that $L/L_0 =$
140 1 at 300 K. Such a tendency of L/L_0 was observed in many cases, e. g. for
141 $\text{La}(\text{Cu}_x\text{Al}_{1-x})_5$ and $\text{Ce}(\text{Cu}_x\text{Al}_{1-x})_5$ compounds [25]. Fig. 6b reveals that at
142 temperatures below about 100 K a strong increase of the deviation from the
143 Wiedemann-Franz law starts and peaks at 9 K, 17 K, 11.5 K and 14 K for
144 CeNi_4Ga , CeNi_4In , CeCu_4Ga and CeCu_4In , respectively. This departure is
145 strongest for CeNi_4Ga and weakest for CeCu_4Ga . The position of the peaks
146 seems to be related directly neither to the CEF nor the Kondo effect.

147 5. Conclusions

148 It has been shown that the temperature dependence of thermopower for
149 the mixed-valence CeNi_4M compounds is negative in the whole temperature

150 range studied and can be satisfactory described assuming two Lorentzian
151 peaks located below and above the Fermi level in the valence band region of
152 DOS. This same simple model with only a single peak, however with the line
153 width dominated by the energy scale set by the crystal electric field provides
154 reasonable values of the Kondo temperatures and CEF splitting for the heavy
155 fermion $CeCu_4M$ compounds. The obtained results are corroborated by the
156 previous electrical resistivity and specific heat studies. Thermal conductivity
157 of the HF compounds differs from the MV compounds mainly by the slope
158 of the temperature dependance.

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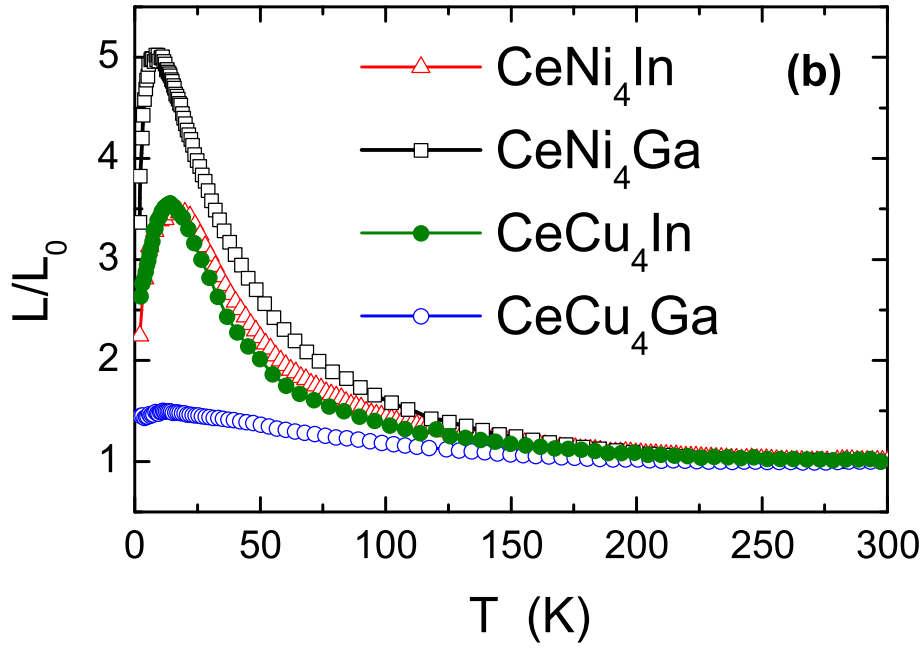
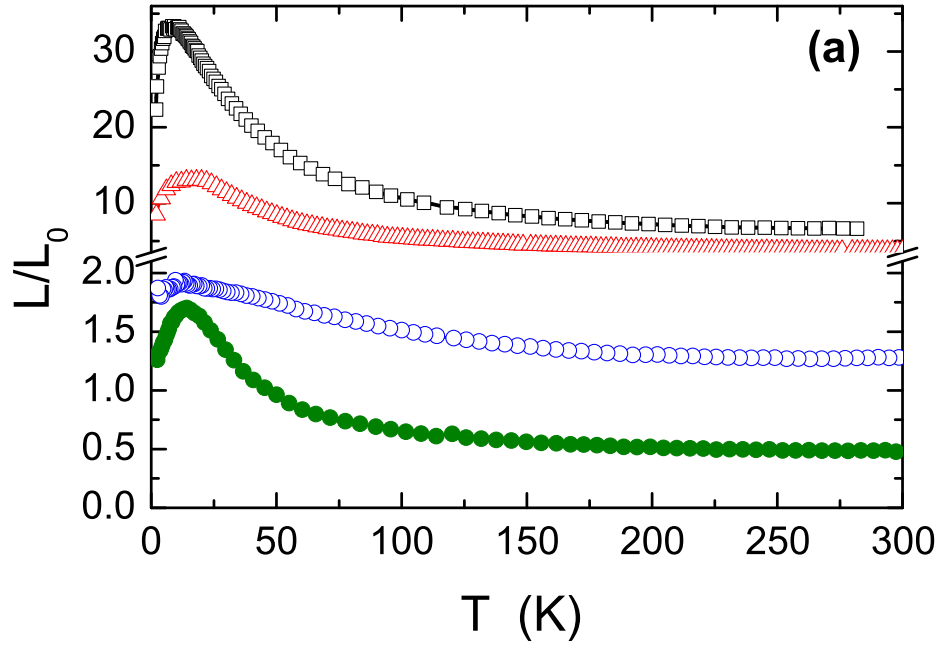


Figure 6: The normalized Lorentz number L/L_0 of the CeCu_4M and CeNi_4M compounds (a) and L/L_0 scaled to 1 at 300 K (b). 12