

# First neutron studies of the magnetism and rattling modes in $\text{CePt}_4\text{Ge}_{12}$

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**Abstract.** The filled skutterudite  $\text{CePt}_4\text{Ge}_{12}$  is reported to be at the border between an intermediate valence (IV) state and a Kondo lattice behavior. We report here the first inelastic neutron scattering experiments, carried out on the Ce compound and its non-magnetic counterpart  $\text{LaPt}_4\text{Ge}_{12}$ . Prior the neutron studies, the structural and magnetic properties of both samples have been determined. Inelastic neutron scattering spectra are dominated by phonon contribution for both compounds. A rattling vibration mode is observed at 6.9 meV and 7.5 meV for the Ce and La compounds, respectively. In  $\text{CePt}_4\text{Ge}_{12}$  no crystal field excitation could be resolved. Only a small and wide extra contribution at high energy (22-28 meV) is observed. This result would be more consistent with an IV behavior.

## 1. Introduction

Rare-earth (RE) filled skutterudites exhibit a large variety of topological magnetic and electrical properties. Recently skutterudites with chemical formula  $\text{MPt}_4\text{Ge}_{12}$  have been synthesized with  $M=\text{Sr, Ba, La, Ce, Pr, Nd}$  and  $\text{Eu}$  [1-3]. Detailed macroscopic measurements on  $\text{CePt}_4\text{Ge}_{12}$  suggest that this compound is at the border between an intermediate valence (IV) and a Kondo lattice behavior [4]. The magnetic susceptibility shows a wide bump around 80 K, typical of IV systems and the Sommerfeld coefficient,  $\gamma=105 \text{ mJ mol}^{-1}\text{K}^{-2}$ , is moderately enhanced compared to those of  $\text{LaPt}_4\text{Ge}_{12}$  and  $\text{PrPt}_4\text{Ge}_{12}$  ( $76 \text{ mJ mol}^{-1}\text{K}^{-2}$  and  $87 \text{ mJ mol}^{-1}\text{K}^{-2}$  respectively [1-3]), but the  $A/\gamma^2$  ratio  $\approx 4 \times 10^{-7} \mu\Omega \text{ cm (mol. K/mJ)}^2$  is far below the universal Kadowaki-Woods relation  $A/\gamma^2=1 \times 10^{-5} \mu\Omega \text{ cm (K mol./mJ)}^2$ . However using the new relation proposed by Tsujii *et al.* [5], who take into account the degeneracy of the quasiparticles, the  $A/\gamma^2$  value becomes closer to the universal value for a degeneracy 6,  $A/\gamma^2=6.4 \times 10^{-6} \mu\Omega \text{ cm (K mol/mJ)}^2$ .

Inelastic neutron scattering (INS) has been proved to be a very original and powerful technique to study heavy fermions and intermediate valence systems [6]. According to previous studies, in case of IV compounds the scattering function has a very particular behavior. At temperatures much lower than the characteristic Kondo energy,  $T_K$  (in IV systems  $T_K$  may vary from 100 up to 700 K), the scattering function presents a wide inelastic structure at high energy. This structure progressively shifts to low energies as the temperature increases and merges into a large quasi-elastic structure, as observed in  $\text{CeSn}_3$  or  $\text{CePd}_3$  [7]. On the other hand in Kondo systems, the Kondo energy is much smaller, of the order of few Kelvins, and the crystal field excitations (CEF) are well resolved.

With the aim to discriminate between intermediate valence or Kondo lattice behavior in  $\text{CePt}_4\text{Ge}_{12}$  we undertook a first study by inelastic neutron scattering. Present results focuses on the inelastic response of  $\text{CePt}_4\text{Ge}_{12}$  and its non-magnetic counterpart  $\text{LaPt}_4\text{Ge}_{12}$ .



## 2. Experimental details

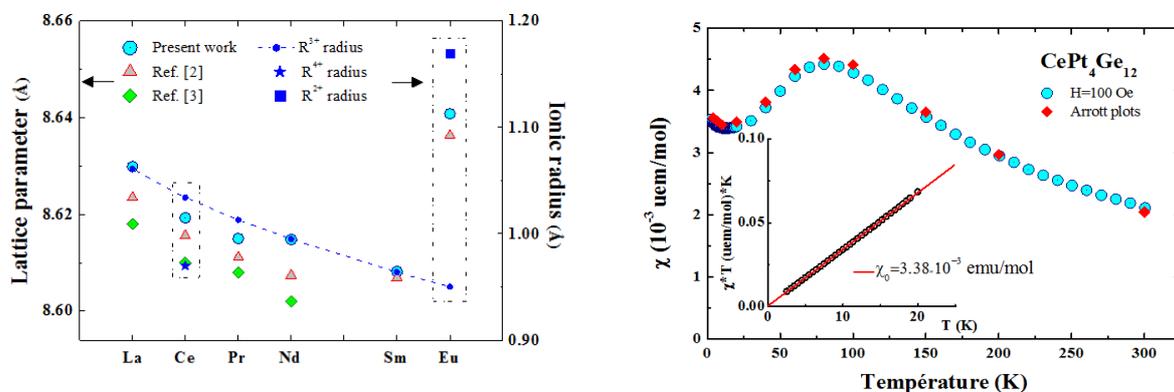
The polycrystalline samples of  $\text{LaPt}_4\text{Ge}_{12}$  and  $\text{CePt}_4\text{Ge}_{12}$ , as well as those of Pr-, Nd-, Sm and  $\text{EuPt}_4\text{Ge}_{12}$ , have been prepared by the conventional induction melting technique. Stoichiometric amounts of high purity elements, 99.9% rare earth, 99.95% Pt, 5N Ge, were melted in a water-cooled copper crucible under a highly purified argon atmosphere. Mass losses were negligible. After this first step, the as-melted samples contain the filled skutterudite phase but also a large amount of impurity phases,  $\text{PtGe}_2$  and Ge. This indicates that the  $\text{RPt}_4\text{Ge}_{12}$  phases are not congruent melting compounds. To achieve the skutterudite phase formation, the samples were sealed in quartz ampoules under high vacuum and annealed at  $780^\circ\text{C}$  for 10 days. The sample quality was checked by powder X-ray diffraction on a Philips PW1730 diffractometer using the  $\text{Cu-K}\alpha$  radiation.

The magnetic measurements were performed on a polycrystalline sample of  $\text{CePt}_4\text{Ge}_{12}$  in the temperature range 1.9 K-300 K and in fields up to 5 T, using a Quantum Design MPMS magnetometer (resolution  $2 \times 10^{-11} \text{ Am}^2$ ). Two types of measurements were carried out, the thermal variation of the magnetization under an applied of  $H=100 \text{ Oe}$  and the variation with the applied field of the isothermal magnetization. The magnetic susceptibility of the compound is deduced from the  $M(100 \text{ Oe}, T)/H$  curve for the first type of measurements and from the Arrott plots [8]:  $M^2=f(H/M)$  for the second one.

Inelastic neutron scattering experiments were carried out with the time-of-flight spectrometer IN4C at ILL on polycrystalline samples of  $\text{LaPt}_4\text{Ge}_{12}$  ( $m=3.93 \text{ g}$ ) and  $\text{CePt}_4\text{Ge}_{12}$  ( $m=3.49 \text{ g}$ ). The incident neutron wavelength was  $\lambda=1.5 \text{ \AA}$  and the full width at half maximum FWHM= $1.7 \text{ meV}$ . Within these conditions, the maximum scattering vector is  $|Q|_{\text{max}}=7.41 \text{ \AA}^{-1}$ . The spectra were collected in the temperature range 2-270 K. The signal is calibrated using a vanadium sample.

## 3. Structural and magnetic properties

The refinements of the X-ray diffraction patterns were performed using the FullProf program [9]. Based on the structure type  $\text{LaFe}_4\text{P}_{12}$ , space group  $Im\bar{3}$ , the lattice parameters of  $\text{LaPt}_4\text{Ge}_{12}$  and  $\text{CePt}_4\text{Ge}_{12}$  are  $8.6299(4) \text{ \AA}$  and  $8.6193(3) \text{ \AA}$  respectively. In rare earth compounds, the lattice parameter is a fairly reliable indicator of the valence state of the rare earth ion. Figure 1 (left) shows the evolution of the lattice parameter from  $\text{LaPt}_4\text{Ge}_{12}$  to  $\text{EuPt}_4\text{Ge}_{12}$ . This evolution is in good consistency with those already reported in the literature for the same  $\text{RPt}_4\text{Ge}_{12}$  series. The evolution of the trivalent ionic radii in the lanthanide series is also reported in figure 1 together with the tetravalent, for Ce, and divalent, for Eu, radii.

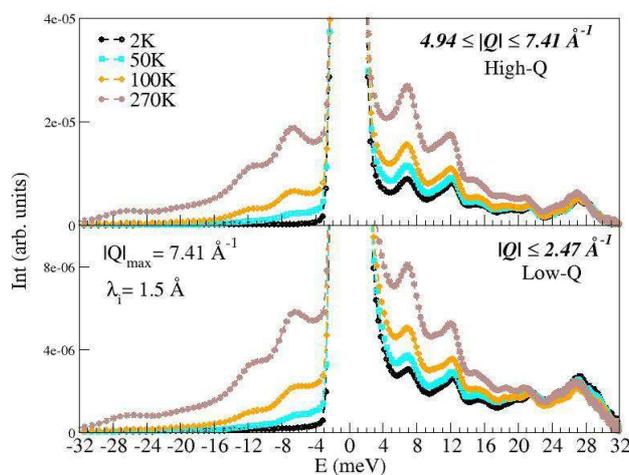


**Figure 1.** Left: evolution of the lattice parameter in the  $\text{RPt}_4\text{Ge}_{12}$  series and comparison with the ionic radii of trivalent R ions (dotted line is a guide for the eyes). The full star represent the ionic radius of  $\text{Ce}^{4+}$  and the full square the radius of  $\text{Eu}^{2+}$  respectively. Right: thermal evolution of the magnetic susceptibility. In inset the curve  $\chi \cdot T=f(T)$ .

It is obvious that the Eu ion is divalent in  $\text{EuPt}_4\text{Ge}_{12}$ . However, within the experimental accuracy, no clear deviation from the trivalent valence is evidenced in  $\text{CePt}_4\text{Ge}_{12}$ . On the other hand the thermal variation of the susceptibility (see figure 1 (right)) is quite consistent with those of Ce-based IV compounds [7]. The susceptibility presents a large bump around 75-80 K, as previously reported in Ref. [4], and a slight increase at low temperatures. In IV systems a Fermi liquid-type behavior is expected at low temperatures leading to a weak but constant susceptibility. The susceptibility increase at low temperatures, observed in many IV systems, is ascribed to a weak amount of paramagnetic impurities. From the curve  $\chi \cdot T = f(T)$ , we determine a Fermi liquid susceptibility  $\chi_0 = 3.38 \times 10^{-3}$  emu/mol.

#### 4. Inelastic neutron scattering

Figure 2 shows the thermal and Q dependences of the INS spectra of  $\text{CePt}_4\text{Ge}_{12}$ . For Ce ions in the 2a site of the  $Im\bar{3}$  space group one expects only one CEF excitation. The expected thermal evolution of such an excitation is a progressive decrease of its intensity with temperature. As seen in figure 2, the INS spectra show several inelastic structures. Two well resolved pics are observed at  $6.9 \pm 0.1$  meV and  $12.1 \pm 0.1$  meV. At higher energies the structures broaden. Less resolved peaks around 15, 18, 21 and 27 meV can be pointed. Moreover, the progressive increase of their intensities with the temperature allows to definitively ascribe these structures to phonon contributions. However one can remark that at low Q and low temperature the INS signal is slightly stronger above 27 meV as expected for a magnetic contribution.

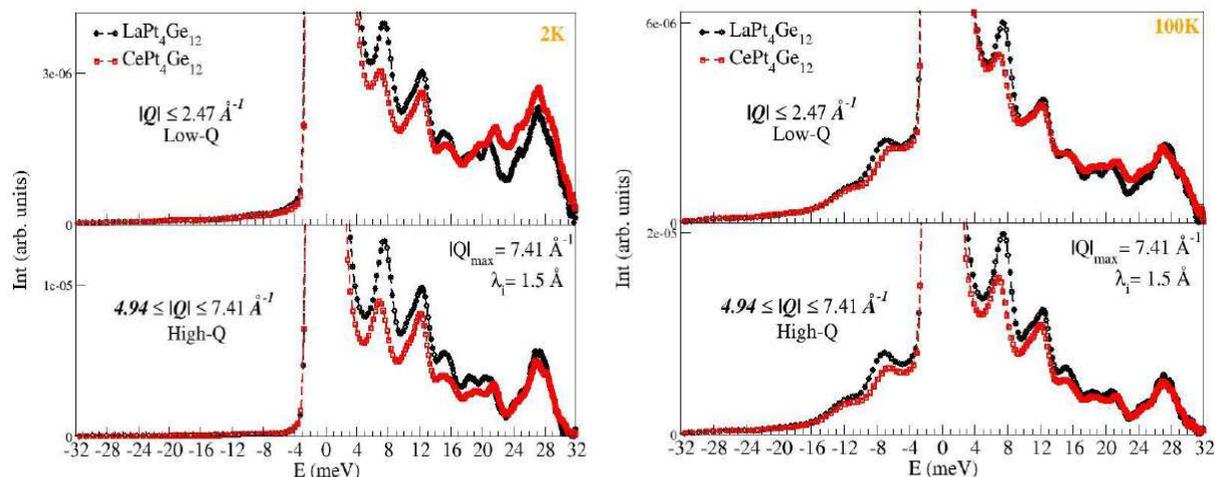


**Figure 2.** Thermal and Q dependences of the inelastic neutron scattering spectra of  $\text{CePt}_4\text{Ge}_{12}$ .

In figure 3 we compare the thermal and Q dependences of the INS spectra of  $\text{CePt}_4\text{Ge}_{12}$  and  $\text{LaPt}_4\text{Ge}_{12}$ . At the first glance  $\text{LaPt}_4\text{Ge}_{12}$  exhibits a behavior very similar to that observed in  $\text{CePt}_4\text{Ge}_{12}$ , confirming the phonon origin of the INS signal. While in the La spectra the second peak is still observed at  $12.1 \pm 0.1$  meV, the first one is slightly shifted to higher energy at  $7.5 \pm 0.1$  meV. The energy of the first peak in the La and Ce compounds is quite consistent with those reported in the literature for other skutterudites families and ascribed to the “rattling” or guest mode [10].

Ab initio phonon simulations reproduce rather well the experimental spectra for both samples and for instance the shift in energy of the low energy peak between La and Ce. Note that in the  $\text{RO}_8\text{Sb}_{12}$  series a similar shift to the lower energies with increasing the atomic number of the rare earth is evidenced [10]. The estimated neutron-weighted partial phonon atomistic contributions bring into evidence that this first peak results essentially from the rare earth ion [11], confirming a rattling

vibration mode. These results will be subject of a forthcoming detailed paper [11]. Nevertheless, as expected for transition metals and rare-earth containing compounds, with active *d*- and/or *f*- shells, respectively, the Ce phonon spectrum is better reproduced by the calculation including the effect of the spin polarization on the lattice, and therefore on the inter-atomic force constants [12].



**Figure 3.** Thermal and Q dependences of the INS spectra of CePt<sub>4</sub>Ge<sub>12</sub> and its non-magnetic counterpart LaPt<sub>4</sub>Ge<sub>12</sub>.

Again at high energy, low Q and low temperature, the intensity of the Ce signal becomes significantly larger than the La one (left upper part in figure 3). This is coherent with the above observation in the lower part in figure 2. This extra and small signal could thus be associated with a large and weak magnetic feature as expected for IV compounds.

## 5. Discussion and Conclusion

The present INS results on CePt<sub>4</sub>Ge<sub>12</sub> clearly confirm that no “normal” CEF excitation exists in the explored energy range, thus excluding a Kondo behavior. The magnetic susceptibility and some features in the Ce spectra (weak and wide signal at high energy) are much more reminiscent of IV compounds. The IV behavior in Ce compounds is generally attributed to a strong hybridization between the 4*f* electron and the conduction band. The behavior of the INS spectra of CePt<sub>4</sub>Ge<sub>12</sub> appears very similar to that of CeOs<sub>4</sub>Sb<sub>12</sub>, where the absence of CEF excitation let suppose delocalised 4*f* electrons [10]. Note that in the ROs<sub>4</sub>Sb<sub>12</sub> series, heavy fermion behaviors have been reported for several compounds. In this last series, the mass enhancement of the conduction electrons has been suspected to be induced by an electron-phonon coupling rather than the “conventionnal” 4*f*-conduction band coupling. Thought the interpretation of combined studies of inelastic X-ray scattering and X-ray absorption spectroscopy in the ROs<sub>4</sub>Sb<sub>12</sub> series is not yet fully achieved, Tsutsui and coworkers [10] conclude that couplings exist between: the guest rattling modes, the 4*f* electrons and the conduction electrons, that may explain, for instance, the heavy fermion behavior of SmOs<sub>4</sub>Sb<sub>12</sub>.

Our results also evidence a “rattling” mode in both the La and Ce compounds but at higher energy (around 7 meV) than in the ROs<sub>4</sub>Sb<sub>12</sub> series (around 3 meV). This indicates that the rare earth ion is more strongly bound to its crystallographic site in the RPt<sub>4</sub>Ge<sub>12</sub> series than in the ROs<sub>4</sub>Sb<sub>12</sub> one. Also the Sommerfeld coefficients reported for La-, Ce- and PrPt<sub>4</sub>Ge<sub>12</sub> have moderate values compared to those in the ROs<sub>4</sub>Sb<sub>12</sub>. Thus, it may be possible that electron-phonon coupling exists in the RPt<sub>4</sub>Ge<sub>12</sub> series, but very likely weaker than in the ROs<sub>4</sub>Sb<sub>12</sub> one. Nonetheless at present time the results on the RPt<sub>4</sub>Ge<sub>12</sub> series are too partial to conclude on the origin of the anomalous behavior of CePt<sub>4</sub>Ge<sub>12</sub>.

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