

CeTPO Compounds: Quasi Two-dimensional Kondo Lattices with Ferromagnetic Correlations

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Since February 2008 the $RTPnO$ (R : rare earth, T : transition metal, Pn : P or As) compounds are at the focus of the solid state physics community due to the discovery of superconductivity with a transition temperature T_c exceeding 50 K in the $RFeAsO_{1-x}F_x$ series [1-4], being the highest T_c except for cuprate systems. This high- T_c superconducting state appears to be unconventional and related to the disappearance of a Fe-based spin density wave. Our interest in these compounds started already in 2003 and is related to our search for ferromagnetic Kondo lattices and the possibility for ferromagnetic quantum critical points in such systems. Kondo lattices and the quantum phase transition from a magnetic ordered to a paramagnetic ground state are the central topics of the Physics department in our Institute. While many Ce-based Kondo lattices show antiferromagnetic (AFM) ground states, only very few systems are known with ferromagnetic (FM) order and pronounced Kondo effects. Therefore, the behavior at a FM critical point in a Kondo lattice is presently not settled [5].

In the process of looking for Ce-based Kondo lattice systems close to a FM quantum phase transition, the CeTPO compound series attracted our interest, due to its rather unusual crystal structure with alternating layers of TP_4 and OCe_4 tetrahedra (Fig. 1). This causes Ce-Ce interatomic distances in the range where FM order could be observed [6]. This compound series, crystallizing in the tetragonal ZrCuSiAs-type structure, was discovered by *Jeitschko* and co-workers [7]; but at the time this project was started, almost no physical properties had been reported. The lattice parameters given in [7] suggested an intermediate valent Ce state in the Fe and Co homologues, but a trivalent one in CeRuPO. We first started with the preparation and investigation of polycrystalline samples of the latter compound [8], thereafter turned to its crystal growth as well as to the study of CeOsPO [8-10], and later to the Fe and Co homologues [11-12]. Here we shall present our

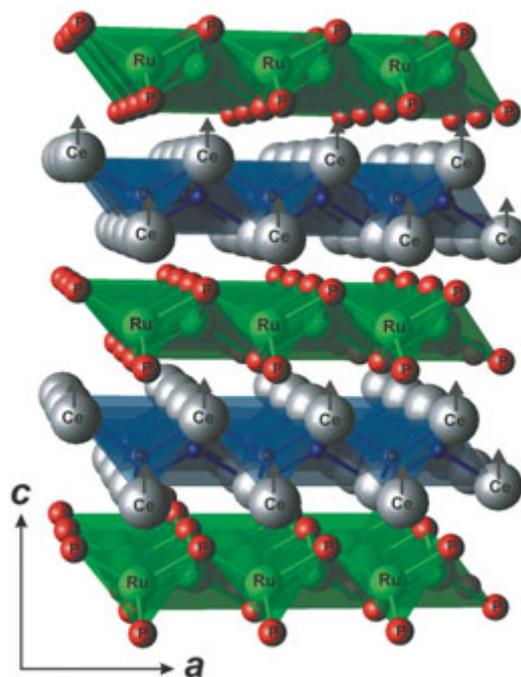


Fig. 1: Tetragonal crystal structure ($P4/nmm$) of the CeTPO compound series, showing the alternating layers of TP_4 and OCe_4 tetrahedra. Arrows illustrate the FM ordering of the Ce-ions in CeRuPO.

main results. Further details as well as the description of the experimental methods can be found in the original publications [8-12].

The polycrystalline samples were prepared using a standard Sn-flux method in evacuated quartz tubes. The preparation was optimized with RuO_2 as the source for oxygen for CeRuPO, while CeOsPO was prepared with SnO_2 instead of the hazardous osmiumtetroxide. Although this method already resulted in very small single crystals, it was not possible to tune the parameter to get single crystals large enough for measurements of physical properties, e.g. bulk susceptibility. We suspected that higher temperatures, above the limitation imposed by quartz, could result in larger single crystals because of higher solubilities. We, therefore, developed a two-step technique, where in the first step P is reacted with Sn in a quartz

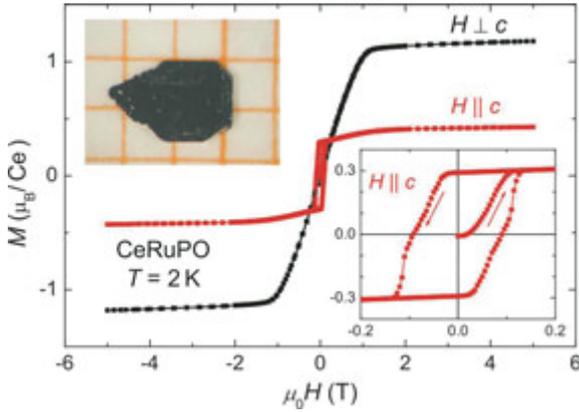


Fig. 2: Magnetization of a CeRuPO single crystal (photograph in the upper inset) for field applied along the basal plane (black symbols) and along the c direction (red symbols). Lower inset enlarges the well defined hysteresis for $H \parallel c$.

tube while the crystal growth itself is performed in an Al_2O_3 crucible sealed into a Ta crucible, which allows to obtain much higher temperatures [9]. By optimizing this method, we obtained CeRuPO single crystals with surfaces larger than 2 mm^2 (cf. inset in Fig. 2), which, despite intensive world wide research, is presently still the largest single crystal size obtained for RTPnO compounds.

CeRuPO indeed turned out to be the anticipated FM Kondo lattice. A trivalent Ce state is evidenced by a Curie-Weiss law in the susceptibility $\chi(T)$ with an effective moment close to that expected for a free Ce^{3+} ion as well as by a large magnetic 4f contribution to the specific heat at low T . FM ordering at $T_C = 15 \text{ K}$ was first indicated by a very large peak in $\chi(T)$ at low fields, but the definitive evidence was provided by the magnetization measurements performed on the single crystal (Fig. 2). The well defined hysteresis with a sizeable saturation moment observed for the field parallel to the c axis establishes a FM state with ordered moments aligned along the c axis (cf. arrows in Fig. 1). The much larger saturation moment observed for fields $\mu_0 H > 1 \text{ T}$ applied within the basal plane confirmed that the crystal electric field (CEF) ground-state doublet bears a larger moment in the plane, as deduced from the anisotropy above T_C . Thus, CeRuPO is one of the rare cases among intermetallic rare-earth compounds where the exchange anisotropy is larger and opposite to the CEF anisotropy, leading to a spontaneous ordering along the hard CEF direction. FM order was also confirmed by the specific heat results, which show a large, lambda-type anomaly at

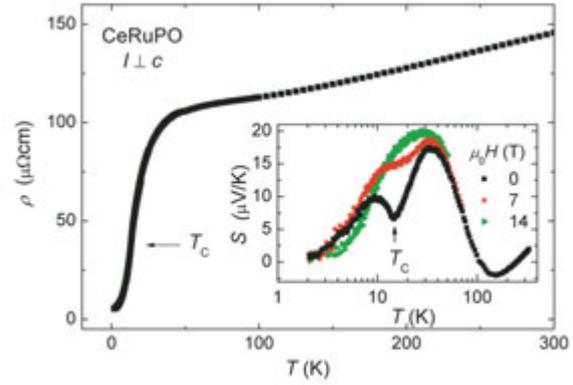


Fig. 3: Temperature dependence of the resistivity of a CeRuPO single crystal for current flowing in the basal plane. T_C marks the FM transition. Inset: thermoelectric power of CeRuPO vs. temperature for different magnetic fields.

T_C , which shifts to higher temperatures and broadens upon applying an external field, as expected for FM ordering.

The presence of a significant Kondo interaction is evidenced by the T dependence of the electrical resistivity $\rho(T)$, which decreases weakly below 300 K down to 50 K, but then drops quite dramatically (Fig. 3). At T_C , which is marked by a kink in $\rho(T)$, the spin disorder scattering as already dropped to less than 40% of its value above 50 K. This kind of pronounced decrease is a hallmark for a Kondo lattice system and related to the onset of coherent Kondo scattering. A significant Kondo interaction is confirmed by measurements of the thermopower $S(T)$ which show large absolute values and the T dependence typical for Kondo lattices (Inset in Fig. 3). The maximum at around 30 K can be attributed to Kondo scattering on excited CEF levels while the maximum (or a shoulder for measurements under applied magnetic field) at lower temperatures is likely related to the Kondo scale. From the T dependence of $\rho(T)$, of $S(T)$, and of the entropy we deduced a Kondo scale of the order of 10 K.

In contrast, our results show that the homologue CeOsPO, despite only minor changes in the lattice parameters, orders antiferromagnetically at $T_N = 4.5 \text{ K}$. Further on in this compound the Kondo interaction seems to be weaker, all the properties indicating rather conventional local moment magnetism.

LDA based band structure calculations evidence a pronounced two-dimensional character of the Fermi surface in both compounds. A slight shift in

the energy of one of the electronic bands resulting in a crossing of the Fermi level along the z direction for Ru while no crossing is predicted for Os is likely responsible for the change from FM to AFM ordering. While CeOsPO on its own does not present interesting properties, a comparative investigation of both compounds provides a meaningful possibility to study the differences between FM and AFM Kondo lattices. ESR measurements performed on both compounds turned out to be the crucial experiment which revealed the relevance of FM correlations for the observability of the ESR line in Kondo lattice systems (see *Electron Spin Resonance of Ferromagnetic Kondo Lattice Systems*) [10].

We synthesized and investigated CeFePO [11]. Both polycrystalline samples and single crystals were prepared using the same techniques as for CeRuPO. We found CeFePO to be a paramagnetic heavy fermion system close to a FM critical point. Below 350 K, $\chi(T)$ increases with decreasing temperature following a Curie-Weiss law down to 100 K (not shown). The effective moment being almost identical to the value expected for a trivalent Ce ion and the moderate Weiss temperature $\theta_W = -52$ K indicate a nearly stable trivalent Ce state and the absence of a significant contribution of a paramagnetic Fe moment in this temperature range. Below 10 K, the measured bulk susceptibility becomes strongly field dependent, showing a pronounced increase for low fields $\mu_0 H < 1$ T, while for larger fields $\chi(T)$ levels off at a constant value $\chi_0 = 660 \cdot 10^{-9} \text{ m}^3/\text{mol}$. Whereas such a field dependence is usually attributed to paramagnetic defects or impurities, the NMR results suggest this to be an intrinsic property of CeFePO (see below). No anomaly corresponding to magnetic order could be resolved at any field. Thus, a preliminary analysis of these susceptibility data suggests a paramagnetic Kondo lattice.

This conclusion is confirmed by the results of the specific heat measurements, plotted as C_{4f}/T vs. T in Fig. 4. The 4f contribution C_{4f} to the specific heat was obtained by subtracting the reported specific heat data of LaFePO [13]. Below 10 K, C_{4f}/T increases logarithmically down to 1 K, where it levels off at a constant value $\gamma = 700 \text{ mJ/molK}^2$. No anomaly indicating a phase transition can be resolved above 0.4 K. Application of a small magnetic field $\mu_0 H < 1$ T does not

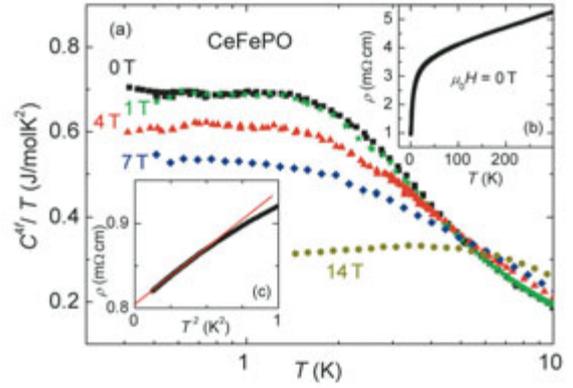


Fig. 4: 4f-increment to the specific heat of CeFePO plotted as C_{4f}/T vs. T in different magnetic fields. Upper inset (b) presents the temperature dependence of the resistivity at higher temperatures. Lower inset (c) shows $\rho \propto T^2$ at low T .

change $C_{4f}(T)$, while a larger field leads to a smooth decrease of C_{4f}/T at low temperatures. The former result confirms the absence of long range magnetic order, while the latter is incompatible with spin-glass-type behavior. Therefore, the large C_{4f}/T value at low T has to be attributed to heavy fermions and corresponds to a strongly enhanced Sommerfeld coefficient. Comparing with the Sommerfeld coefficient of the nonmagnetic LaFePO (12.5 mJ/molK^2) [13], one estimates a low-temperature enhancement factor of the order of 50 for the heavy quasiparticles in CeFePO. The magnetic entropy was calculated by integrating the measured $C_{4f}(T)/T$ over T for $T < 10$ K. The entropy reaches $0.5 \cdot R \ln 2$ at 5 K, indicating a Kondo temperature $T_K \approx 10$ K. The absolute values of $C(T)$, its temperature dependence as well as the deduced Kondo temperature are very close to those of the archetypical heavy fermion metal CeCu₂Si₂ [14].

The temperature dependence of the electrical resistivity $\rho(T)$ shown in the inset (b) of Fig. 4 presents the typical behavior of a Kondo lattice system and, thus, confirms the above conclusions. Below 300 K, $\rho(T)$ decreases almost linearly, before dropping rapidly below 30 K due to the onset of coherent Kondo scattering. Below 1 K [see inset (c)] $\rho(T)$ follows a $\rho \propto T^2$ dependence indicating the formation of a Landau-Fermi liquid ground state in agreement with the specific heat data. However, the Sommerfeld-Wilson ratio χ/γ is significantly larger than expected for a Kondo lattice pointing to FM correlations.

The conclusions drawn from the magnetic, transport and thermodynamic measurements were confirmed by the results of microscopic measurements using ^{31}P -NMR as a local probe. We first focus on the temperature dependence of the relaxation time T_1 shown in the main part of Fig. 5: For Kondo systems, one expects $1/T_1T$ to increase proportional to $1/\sqrt{T}$ upon decreasing temperatures and to merge in a strongly enhanced constant value at low T due to the formation of the heavy quasiparticles. This is indeed what we observed in CeFePO. $^{31}(1/T_1T)$ increases monotonously by two orders of magnitude upon cooling from 300 K to 4 K and then merges into a constant value, which is much larger than that observed in homologue La compounds. Our experimental data compare very well with calculations based on simple standard models for Kondo lattices (red line in Fig. 5). Furthermore, we compare $^{31}(1/T_1T)$ of CeFePO with ^{29}Si -NMR results of the prototypical heavy fermion metal CeCu_2Si_2 [15] which has a similar Kondo scale (inset of Fig. 5). The data were normalized in such a way as to allow for a comparison on an absolute scale (for details see [11]). Both curves share the same overall temperature dependence but CeFePO shows larger absolute values. The very similar T-dependences found for CeFePO and CeCu_2Si_2 hint at similar spin-fluctuation relaxation mechanisms in both compounds and confirm that the strong correlation effects in CeFePO originate from the Ce- $4f$ electrons rather than from Fe-3d electrons.

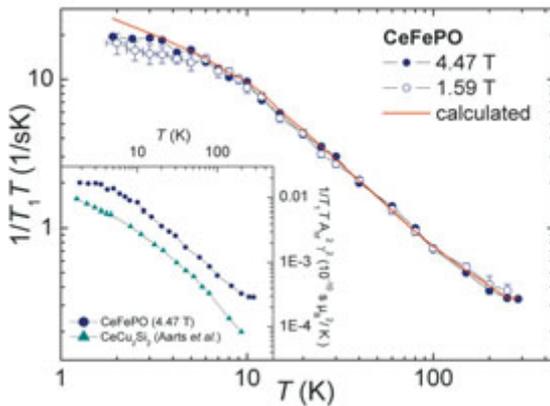


Fig. 5: $^{31}(1/T_1T)$ as a function of temperature for different fields as indicated. Solid line represents the calculation described in the main text. Inset shows the comparison with ^{29}Si -NMR results on CeCu_2Si_2 (data taken from Ref. [15]).

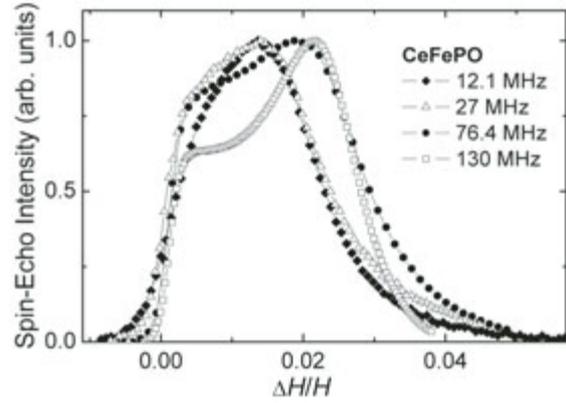


Fig. 6: ^{31}P field-sweep NMR spectra at 2 K and different frequencies (i.e. magnetic fields), showing the change of the line shape as a function of applied field.

An interesting feature was observed in the NMR line shape at low temperatures (Fig. 6). We observed a strong field dependence, with an asymmetric line broadening at a lower field. This is an indication for the presence of strong ferromagnetic correlations, indicating this system to be close to a ferromagnetic critical point.

In summary, we started detailed investigation of the CeTPnO systems. We prepared polycrystals of CeFePO, CeRuPO and CeOsPO and grew single crystals of the two former ones. The compounds were investigated by means of susceptibility, specific heat, resistivity, thermopower and NMR measurements. While CeOsPO is a rather conventional local-moment Ce compound with AF order, CeRuPO is a rare example of a ferromagnetic Kondo lattice system. CeFePO seems to be on the paramagnetic side of the quantum critical point associated with the disappearance of a FM state. It presents a paramagnetic heavy fermion state with a strongly enhanced Sommerfeld coefficient $\gamma = 700 \text{ mJ/molK}^2$ and evidence for strong FM correlations.

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