Structural and Physical Properties of New Rare-Earth Compounds $RE_2Ni_{36}P_{15}$, *RE* = La, Ce, Pr

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In the search for new materials with unconventional ground states we have investigated new phosphides $\boldsymbol{RE}_2Ni_{36}P_{15}$ (***RE*** = La, Ce, Pr). This report presents their structural and physical properties. It will be seen that the Ce containing phase have the characteristic properties observed for heavy fermion systems where the magnetic moments are Kondo screened by the charge carriers.

The $\boldsymbol{RE}_2Ni_{36}P_{15}$ compounds were prepared by a pre-reaction of compacted mixtures from rare-earth metal filings, nickel powder and red phosphorus in a carbon-glass crucible inside an evacuated silica tube with subsequent arc re-melting and annealing at 1173 K.

A single crystal of $Ce_2Ni_{36}P_{15}$ with linear dimensions 0.08 × 0.06 × 0.05 mm^3 was chosen for X-ray structure determination: space group ***Pnma***, ***R***(***F***) = 0.042 for 1727 symmetry independent reflections ($\boldsymbol{F} > 4\sigma F$) and 141 refined parameters. The other two phases $(La,Pr)_2Ni_{36}P_{15}$ were characterized with X-ray powder diffraction (Image Plate Huber Guinier camera, $CuK\alpha_1$ radiation) and found to be isostructural to $Ce_2Ni_{36}P_{15}$. The obtained lattice parameters (see table 1) reveal the unit cell volume of the cerium phase as expected from the lanthanide contraction.

Compound	***a*** [Å]	***b*** [Å]	***c*** [Å]
$La_2Ni_{36}P_{15}$	12.3416(1)	15.2203(1)	6.69129(6)
$Ce_2Ni_{36}P_{15}$	12.3129(1)	15.2083(2)	6.69136(7)
$Pr_2Ni_{36}P_{15}$	12.2981(1)	15.1983(1)	6.69128(5)

Tab. 1: Lattice parameter for $RE_2Ni_{36}P_{15}$.

In the structure of $Ce_2Ni_{36}P_{15}$, nickel and phosphorus atoms form a three dimensional network where the nickel atoms have 2-4 nearest phosphorus neighbors and the phosphorus atoms have only nickel as nearest ligands (CN = 8 – 12). The network has four relatively large cavities per unit cell which are occupied by the cerium atoms (Fig. 1).

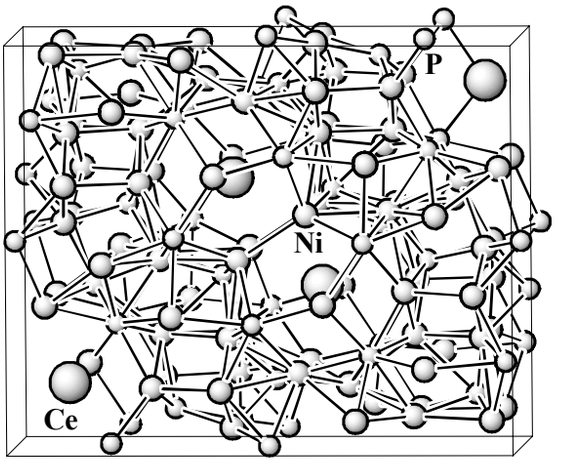

Fig. 1: 3D-Network of nickel and phosphorus atoms with the cavities filled by cerium in the crystal structure of $Ce_2Ni_{36}P_{15}$.

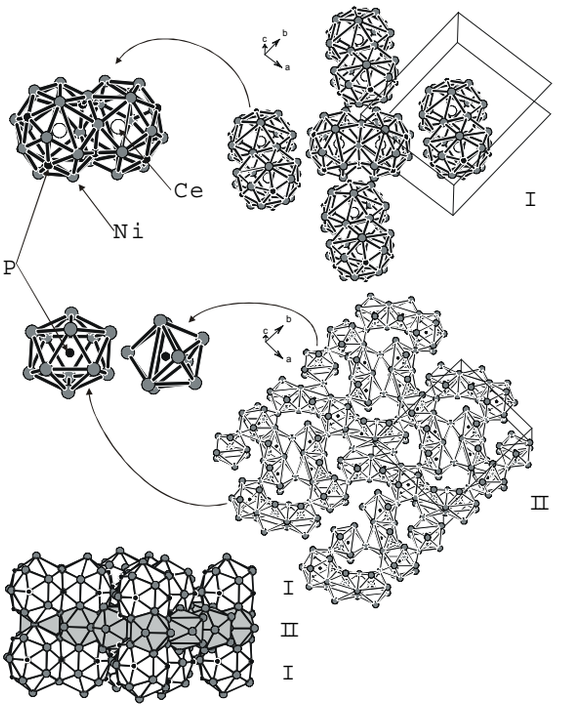

Fig. 2: Structural fragments in $Ce_2Ni_{36}P_{15}$.

The whole structure can be approximated by two different layers (Fig. 2). The first (I in Fig. 2) consists of network fragments around the cerium atoms. The second (II in Fig. 2) is formed by nickel and phosphorus atoms only. The cavities containing cerium atoms are each built by 22 atoms (16 Ni and 6 P) and form pairs connected through a lateral six-edge face. With respect to the cerium atoms the special structural features of $Ce_2Ni_{36}P_{15}$ are: i) very low concentration of cerium in the material; and ii) pair-clustering of cerium in the structure with ***d***(Ce-Ce) = 4.15 Å.

^{31}P-MAS-NMR measurements on $La_2Ni_{36}P_{15}$ and $Ce_2Ni_{36}P_{15}$ (Fig. 3) confirmed the ordered distribution of phosphorus in the structure: In $La_2Ni_{36}P_{15}$ seven different isotropic chemical shifts related to crystallographic phosphorus positions were identified. For $Ce_2Ni_{36}P_{15}$ these lines were shifted to lower and broadened, most likely caused by the magnetic ions in this compound. Because of the reduced resolution the assignment of the isotropic values of the chemical shift was difficult and not unambiguous in any case.

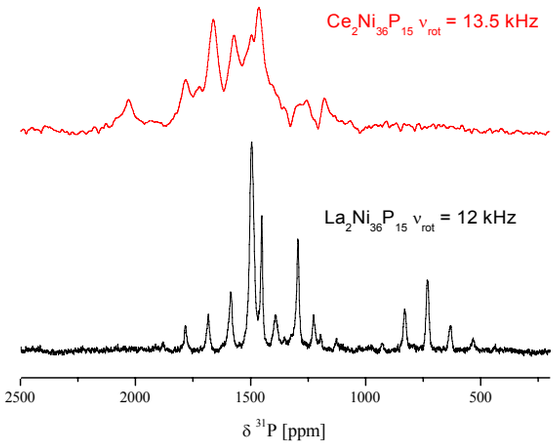

Fig. 3: ^{31}P-MAS-NMR spectrum of $La_2Ni_{36}P_{15}$ and $Ce_2Ni_{36}P_{15}$.

Figure 4 shows the resistivity (ρ) of the La, Ce and Pr compound measured in magnetic fields of 0 T and 13 T, as a function of temperature. All compounds reveal a metal-like behavior with a positive temperature coefficient ($\delta\rho/\delta\boldsymbol{T}$), with exception of $Ce_2Ni_{36}P_{15}$ in the temperature range from 2 K to 14 K where $\delta\rho/\delta\boldsymbol{T}<0$ for ρ measured at 0 T. The $\rho(\boldsymbol{T})$ characteristics of $La_2Ni_{36}P_{15}$ and $Pr_2Ni_{36}P_{15}$

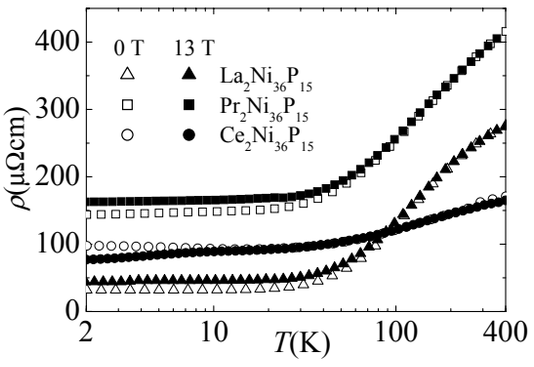

Fig. 4: ρ as function of temperature measured in 0 T and 13 T magnetic fields.

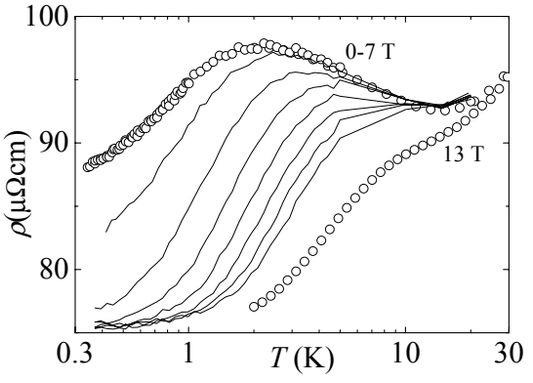

Fig. 5: ρ as function of temperature for $Ce_2Ni_{36}P_{15}$.

are very similar to each other, although $Pr_2Ni_{36}P_{15}$ apparently has a large residual resistance. In contrast, $\rho(\boldsymbol{T})$ for $Ce_2Ni_{36}P_{15}$ behaves differently. The residual resistance ratio is smaller and a negative magnetoresistance is observed at low ***T***.

Because of the negative $\delta\rho/\delta\boldsymbol{T}$ of $Ce_2Ni_{36}P_{15}$, $\rho(\boldsymbol{T},\mu_0\boldsymbol{H})$ has been investigated in more detail and to lower temperatures. Fig. 5 shows $\rho(\boldsymbol{T})$ in the range from 0.4 K to 20 K with magnetic fields varied in 1 T steps from 0 T to 7 T. Included are also the data from Fig. 4. In 0 T a minimum in $\rho(\boldsymbol{T})$ is observed at approximately 15 K and $\rho(\boldsymbol{T})$ increases approximately logarithmically down to 3 K. This is followed by a maximum at approximately 2 K and an almost linear decrease down to 0.4 K.

As the magnetic field is increased $\rho(\boldsymbol{T})$ decreases and, at approximately 6 to 7 T, the minimum in $\rho(\boldsymbol{T})$ has vanished. This is the type of behavior typically observed in heavy fermion systems.

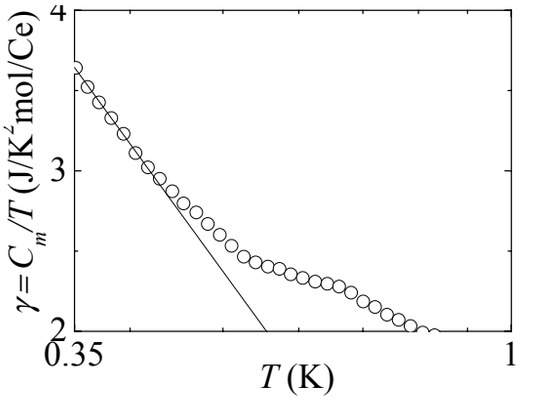

Fig. 6: Sommerfeld coefficient for $Ce_2Ni_{36}P_{15}$ as function of temperature. The solid line is a fit to $\gamma = a + b \log T$.

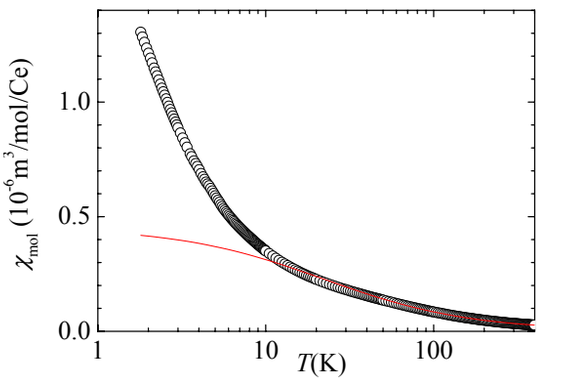

Fig. 7: Magnetic susceptibility as function of temperature for $Ce_2Ni_{36}P_{15}$.

Taking $La_2Ni_{36}P_{15}$ as a nonmagnetic reference compound we determined the magnetic contribution to the specific heat of $Ce_2Ni_{36}P_{15}$ as $\boldsymbol{C}_m = \boldsymbol{C}(Ce_2Ni_{36}P_{15}) - \boldsymbol{C}(La_2Ni_{36}P_{15})$. The result is seen in Fig. 6 where the Sommerfeld coefficient ($\gamma = \boldsymbol{C}_m/\boldsymbol{T}$) is plotted as function of temperature. γ increases monotonically as $\boldsymbol{T}$ decreases and, below approximately 0.43 K, $\gamma = \boldsymbol{a} + \boldsymbol{b} \log \boldsymbol{T}$ holds, as can be seen from the solid line in Fig. 6. This is also a typical behavior of a heavy fermion system. From ρ and $\boldsymbol{C}_p$ the Kondo temperature ($\boldsymbol{T}_K$) can be estimated to approximately 1.8 K. γ for $Ce_2Ni_{36}P_{15}$ is several hundred times larger than for the reference compound $La_2Ni_{36}P_{15}$ pointing to an extremely large effective mass of the quasiparticles.

The temperature dependence of the magnetic susceptibility $\chi(\boldsymbol{T})$ (Fig. 7) does not provide any evidence for magnetic ordering at low temperatures. Data above 100 K have been fitted to a Curie-Weiss type equation where μ_{eff} = 2.51 μ_B/Ce is close to the theoretical value of 2.54 μ_B for free Ce^{3+}. The corresponding fitted Weiss temperature is -22 K. At low temperatures $\chi(\boldsymbol{T})$ increase approximately logarithmically.

In this report we have shown the structural and physical properties of some new compounds where ***RE***-atoms are enclosed in cages. $La_2Ni_{36}P_{15}$ and $Pr_2Ni_{36}P_{15}$ can be regarded as normal metals whereas $Ce_2Ni_{36}P_{15}$ is a heavy fermion system with $\boldsymbol{T}_K \sim 1.8$K.