Valence fluctuation and magnetic ordering in EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$ single crystals

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Abstract

Unusual phases and phase transitions are seen at the magnetic–nonmagnetic boundary in Ce-, Eu- and Yb-based compounds. EuNi$_2$P$_2$ is a very unusual valence fluctuating Eu system, because at low temperatures the Eu valence stays close to 2.5 instead of approaching an integer value. The Eu valence, and thus the magnetic property in this system, can be tuned by Ge substitution in the P site as EuNi$_2$Ge$_2$ is known to exhibit the antiferromagnetic (AFM) ordering of divalent Eu moments with $T_N = 30$ K. We have grown EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$ (0.0 $\leq$ $x$ $\leq$ 0.5) single crystals and studied their magnetic, thermodynamic and transport properties. Increasing Ge doping to $x > 0.4$ results in a well-defined AFM ordered state with $T_N = 12$ K for $x = 0.5$. Moreover, the reduced value of magnetic entropy for $x = 0.5$ at $T_N$ suggests the presence of valance fluctuation/the Kondo effect in this compound. Interestingly, the specific heat exhibits an enhanced Sommerfeld coefficient upon Ge doping. Subsequently, electronic structure calculations lead to a non-integral valence in EuNi$_2$P$_2$ but a stable divalent Eu state in EuNi$_2$Ge$_2$, which is in good agreement with the experimental results.

Keywords: valence fluctuation, heavy fermion, Kondo effect, magnetic order

(Some figures may appear in colour only in the online journal)

1. Introduction

Recent decades abound with research on strongly correlated systems with inner $f$-electron shell instabilities, mainly due to the wide range of fascinating phenomena that have been discovered in these systems, such as ‘heavy-fermion (HF) superconductivity’, Kondo insulators, valence fluctuation (VF), non-Fermi liquid (NFL) behavior, quantum criticality etc [1]. Moreover, long-range magnetic ordering in the system can be destabilized by tuning the external or internal (alloying) pressure, or by the application of an external magnetic field leading the system to the borderline between magnetically ordered and nonmagnetic ground states. The precarious point of instability between two stable phases of matter, which is the playground of new interesting physics, is called the ‘quantum critical point’ (QCP). In addition to this, valence instability, which is prone to occur near the middle of the lanthanide series, is a key factor governing the ground state and can also lead the system to the QCP. While most experimental and theoretical efforts have been focused on the elements Ce and Yb, [2] Eu compounds are relatively unexplored.

Similar to Ce- and Yb-based systems, one can tune the electronic ground state of Eu compounds. However, the evolution of the valence $v$ of Eu-based systems as a function of temperature $T$ and composition $x$ or pressure $p$ differs strongly from the phase diagrams for Ce or Yb systems. In Ce or Yb systems, increasing the hybridization results in a smooth and continuous evolution of $v$ as a function of $p$ or $x$ and the magnetic ordering temperature $T_N$ decreases continuously to a zero value at a quantum critical point [3, 4]. On the other hand, for Eu-based systems, increasing hybridization leads to a slight increase in $T_N$ rather than a decrease. At a critical value, an abrupt transition to an almost trivalent Eu ground state occurs.

The characteristic phase diagram for Eu systems was first established in the system Eu(Ut$_{1-x}$Au$_x$)$_2$S$_2$ [5], and was later confirmed in Eu(Pt$_{1-x}$Ni$_x$)$_2$S$_2$ [6]. Substituting Ni for Pt in EuPt$_2$S$_2$ acts as a chemical pressure in the system and suppresses antiferromagnetism (AFM) completely. More recently,
the substitution of Si in EuCu2Ge2 was shown to be of particular interest because the rare-earth ion configuration changes from a nearly integral valence Eu2+(4f7) in antiferromagnetic EuCu2Ge2 to a valence fluctuating state in EuCu2Si2. A strong electron mass enhancement was reported in the compounds near the crossover from a magnetic to non-magnetic state [7]. One striking feature of this system is the coexistence of the magnetically ordered phase with valence fluctuations [7, 8]. We present the crystal growth of EuNi2(P1−xGe)x2 and study the evolution from valence-fluctuating EuNi2P2 to divalent Eu upon increased Ge doping. One advantage of substituting Ge for P, instead of e.g. Fe for Ni, is that both EuNi2P2 and EuNi2Ge2 crystallize in the so-called ‘collapsed structure’, while substituting Fe for Ni results in a change from a collapsed to a non-collapsed structure, for which one can expect a strong disorder effect.

The compound EuNi2P2 exhibits valence fluctuating behavior and possesses a gradual change of Eu valence with decreasing temperature [9, 10]. The temperature dependence of the Eu valence was also probed by Mössbauer spectroscopy, where the isomer shift gradually moves with a decreasing temperature from −6.4 mm s−1 at room temperature to −4.4 mm s−1 at 4.2 K [11]. A photoemission spectroscopy study on high-quality single crystals of EuNi2P2 revealed the presence of heavy bands in the compound [12]. On the other hand, isostructural EuNi2Ge2 [13] exhibits a stable divalent Eu state which orders antiferromagnetically at 30.8 K. Anticipating the fact that Ge substitution for P in EuNi2P2 may change the magnetic ground state of Eu, and the system may exhibit quantum critical behavior at the magnetic–nonmagnetic borderline, we have carried out a systematic study of the EuNi2(P1−xGe)x2 system.

2. Methods

We have grown the single crystals of EuNi2(P1−xGe)x2 using Sn-flux. The starting elements Eu, Ni, (P1−xGe)x and Sn were taken in the ratio of 2:1:1.2:5 and the mixture was placed in an alumina crucible and subsequently sealed in an evacuated quartz ampoule. The sealed quartz ampoule was slowly heated to 1050 °C and held at that temperature for 20h for proper mixing. It was then cooled down at a rate of 2 °C h−1 down to 500 °C and rapidly brought down to room temperature in 2h. The single crystals were removed by etching the Sn-flux with diluted HCl. We obtained plate-like single crystals of different sizes depending on the Ge concentration varying from 4 × 4 × 0.2 mm3 to 2 × 2 × 0.1 mm3. The samples were characterized by powder x-ray diffraction with Cu-Kα radiation to determine the phase purity and crystal structure. We studied the compositional homogeneity for the EuNi2(P1−xGe)x2 samples using a scanning electron microscope (SEM) equipped with energy dispersive x-ray (EDX) analysis.

3. Results and discussion

3.1. Crystal structure

Figure 1 shows the x-ray diffraction pattern of the EuNi2(P1−xGe)x2 (x = 0, 0.1, 0.3, 0.4 and 0.5) plate-like single crystals. We observe only the (00l) reflections which indicate that the c-axis is perpendicular to the crystal plane. For the crystals with a concentration of Ge above 30%, two small extra x-ray peaks appear at around 31°, which come from the tiny unreacted Ni-Sn phase attached to the surface of the crystals. SEM images for the 40% and 50% Ge-doped samples also reveal a few tiny scattered unreacted Ni-Sn alloy flakes attached to the surface of the crystals. Upon increasing the Ge concentration, the (00l) peaks monotonically shift toward a lower 2θ angle, indicating a continuous increase in the c-axis lattice parameter with increasing x, suggesting less hybridization between the Eu layer and the Ni-P, Ge layer. The other lattice parameter a = b was calculated through powdered x-ray diffraction on the crushed single crystals. Analysis of the powder x-ray diffraction data revealed that all the compounds EuNi2(P1−xGe)x2 crystallize in a ThCr2Si2-type tetragonal crystal structure (space group I4/mmm). The obtained lattice parameters for EuNi2P2 are in close agreement with the values reported in the literature [9]. The c-axis
lattice parameter increases anisotropically with an increasing Ge doping concentration.

3.2. Magnetization

The temperature-dependent magnetic susceptibilities for EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$ ($0 \leq x \leq 0.5$) are shown in figure 2. At higher temperatures, the susceptibility follows modified Curie–Weiss (CW) law: $\chi(T) = \chi_0 + C/(T - \theta)$, where $C$ is the Curie constant and $\theta$ is the Curie–Weiss temperature. The calculated effective magnetic moment $\mu_{eff} = 6.9 \mu_B$/Eu for EuNi$_2$P$_2$ lies in between the values for Eu$^{2+}$ and Eu$^{3+}$. The effective moments increase slightly with an increasing Ge content up to $x = 0.4$. However, the values are still smaller than $\mu_{eff} = 7.94 \mu_B$/Eu for a stable divalent Eu$^{2+}$ ion. The shapes of the magnetic susceptibilities of EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$ with $0 \leq x \leq 0.4$ (figure 3) are typical of those for valence-fluctuating Ce compounds [14–18], where sometimes the magnetic susceptibility shows a Curie tail at lower temperatures [17, 19], which arises due to the presence of a magnetic impurity.

Sales and Wohlleben developed a model (interconfiguration fluctuation model, ICF) addressing this behavior [20–22]. The model says that overall magnetic susceptibility can be described by the sum of three different parts: a valence fluctuation part, a part for stable Eu$^{2+}$ (including the trace amounts of possible impurities) and a temperature-independent part. Thus, the temperature dependence of the susceptibility is given by

$$\chi(T) = \left(\frac{N}{3k_B}\right) \left[\mu_n^2 \nu(T) + \mu_{n-1}^2 \left(1 - \nu(T)\right)\right] + f \frac{C}{T - \theta} + \chi_0$$

with

$$\nu(T) = \frac{2J_n + 1}{(2J_n + 1) + (2J_{n-1} + 1) \exp(-E_{ex}/k_BT)}$$

and

$$T^* = [T + T_{sd}]$$

where $\mu_n$ and $\mu_{n-1}$ are the effective moments in the 4$f^n$ and 4$f^{(n-1)}$ states, $(2J_n + 1)$ and $(2J_{n-1} + 1)$ are the degeneracies of the corresponding energy states $E_n$ and $E_{n-1}$. In these expressions, $E_{ex}$ is the interconfigurational excitation energy, which is equal to $(E_{0n} - E_{01})$, where the Eu$^{3+}$ ($E_{0n}, J_n = 0$ and $\mu = 0 \mu_B$) state is the ground state and Eu$^{2+}$ ($E_{0n-1, J_{n-1}} = \frac{2}{7}$ and $\mu = 7.94 \mu_B$) is the excited state. $T_{sd}$ is the spin fluctuation temperature associated with the valence fluctuation, and $f$ is the fraction of stable Eu$^{2+}$ ions responsible for the CW behavior. Thus the final equation is

$$\chi(T) = \left(\frac{N}{3k_B}\right) \left[\left(\frac{7.94 \mu_B}{T^*}\right)^2 \left(1 - \nu(T)\right)\right] + f \frac{C}{T - \theta} + \chi_0$$

The solid line through the magnetic susceptibility data in figure 3 is the fit to the equation 4. The values of parameters obtained from the least square fits are listed in table 2. The values of $f$ (0.02–0.2), $E_{ex}$ and $T_{sd}$ are in the typical range of values found for another valence-fluctuating system: Eu$_{1-x}$La$_x$Pd$_3$ ($E_{ex} = 418$ K and $T_{sd} = 164$ K) [23]. However, the values of excitation energies and spin fluctuation temperatures are found to increase with an increasing $x$, which is inconsistent with our finding that the system attains a stable magnetically ordered state with increased Ge-doping. This inconsistency might arise due to the fact that for EuNi$_2$P$_2$ one needs to include on-site Coulomb repulsion ($U_{bd}$) between the 4f and 5d electron, i.e. the Falikov–Kimball term along with hybridization ($V_{ij}$) between 4f and the valence electrons. However, such analysis is not possible at this juncture as an evolution of $U_{bd}$ with $x$ is not known.

For the 50% Ge-doped sample, the effective paramagnetic moment is very close to that of a free Eu$^{2+}$ ion (4$f^7$; $S = 7/2$, $L = 0$, and $J = 7/2$). Also, a susceptibility peak corresponding to the transition to an antiferromagnetic state occurs at $T_N = 12$ K for $x = 0.5$, confirming that the system evolves from a valence-fluctuating state to a d Avalent state of Eu upon increased Ge concentration. To further elucidate the magnetic properties, we carried out high-field isothermal magnetization measurements at temperatures of 2 K and 18 K,

![Figure 3](image-url)
Table 2. Effective paramagnetic moments $\mu_{\text{eff}}$ ($\mu_B$), interconfiguration excitation energy $E_{\text{ex}}$ (K), spin fluctuation temperature $T_{\text{sf}}$ and antiferromagnetic ordering temperature $T_N$ (K) of EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$.

| $x$  | $\mu_{\text{eff}}$ ($\mu_B$) | $E_{\text{ex}}$ (K) | $T_{\text{sf}}$ (K) | $T_N$ (K) |
|------|-------------------------------|---------------------|---------------------|-----------|
| 0    | 6.9                           | 192                 | 53                  | —         |
| 0.1  | 7.2                           | 227                 | 77                  | —         |
| 0.3  | 7.7                           | 274                 | 91                  | —         |
| 0.4  | 7.8                           | 333                 | 81                  | —         |
| 0.5  | 8.0                           | —                   | —                   | 12        |
| 1.0  | 8.0                           | —                   | —                   | 30.8      |

with an applied field $H$ parallel to the $ab$ plane of the crystals. As shown in figure 4(a), for a lower doping concentration of Ge up to 40%, the magnetization increases linearly with the field. Also, the slope of the lines becomes steeper as we increase the Ge doping concentration, indicating the increase in the paramagnetic moment. For EuNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$, the magnetization varies almost linearly with the field in the range 0 Oe $\leq H \leq$ 20 kOe, accompanied by a change in the slope at $H_c \approx$ 20 kOe, indicating a spin flop-like transition, which is usual for antiferromagnets. As shown in figure 4(b), the $M(H)$ isotherm for EuNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$ exhibits a spin flop transition for $T \leq T_N$ while $M$ varies linearly with $H$ above the magnetic ordering temperature.

3.3. Specific heat

The temperature dependencies of the specific heat $C_p(T)$ of the series are displayed in figure 5. For $x \leq 0.3$, the specific heat exhibits no anomaly down to 2 K and hence confirms the absence of any magnetic ordering. When we plot the $C_p(T)/T$ versus $T^2$ data (inset of figure 5), a linear region is observed below 10 K for $x = 0$ and 0.1. The low temperature data of $C_p(T)/T$ versus $T^2$ below 10 K is fitted to the equation

$$C_p(T)/T = \gamma + \beta T^2$$

(6)

where the $\gamma T$ term is the contribution of the conduction electrons and the $\beta$ term reflects the phonon contribution to the specific heat. The fit to the data yields the value of $\gamma = 98$ mJ mol$^{-1}$ K$^{-2}$ and $\beta = 4.6 \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$ for EuNi$_2$P$_2$. The obtained value of Sommerfeld coefficient for EuNi$_2$P$_2$ is in good agreement with the literature [9]. Furthermore, we estimate the Debye temperature $\Theta_D$ for EuNi$_2$P$_2$ from $\beta$ using the relation [24]

$$\Theta_D = \left(\frac{12\pi^2 n R}{5\beta}\right)^{1/3}$$

(7)

where $R$ is the molar gas constant and $n = 5$ is the number of atoms per formula unit (f.u.). We obtain the Debye temperature $\Theta_D = 276$ K for EuNi$_2$P$_2$. For the 10% Ge substituted sample EuNi$_2$(P$_{0.9}$Ge$_{0.1}$)$_2$, we observe an enhanced Sommerfeld coefficient of $\gamma = 130$ mJ mol$^{-1}$ K$^{-2}$, indicating an effective mass enhancement for the conduction electrons in the valence-fluctuating regime. For $x = 0.3$ the $\beta$ coefficient remains the same ($4.6 \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$), but the Sommerfeld coefficient increases significantly ($\gamma = 185$ mJ mol$^{-1}$ K$^{-2}$). However, the estimation of the Sommerfeld coefficient ($\gamma$) for $x = 0.3$ may not be reliable as a slight deviation is seen in the $C_p(T)/T$ versus $T^2$ curve below 2.25 K, the origin of which is not yet understood. Although heavy fermion behavior has been observed in many Ce-based compounds, there are very few examples of Eu-based heavy fermion compounds [7]. For $x = 0.5$, a broadened mean field-type transition is observed at $T_N = 12$ K corresponding to the antiferromagnetic transition and hence confirming the intrinsic and bulk nature of the magnetic ordering.

In order to isolate the magnetic contribution to the specific-heat $C_{\text{mag}}(T)$, $C_p(T)$ data for the isostructural nonmagnetic reference compound LaNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$ was used from [25]. Figure 6 shows the temperature dependence of the heat capacity of EuNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$, together with the heat capacity of nonmagnetic reference polycrystalline LaNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$. The magnetic part of the heat capacity $C_{\text{mag}}(T)$ was deduced...
by the usual method of subtracting the heat capacity of LaNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$ from that of EuNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$ after adjusting the renormalization due to different atomic masses of La and Eu. The magnetic contribution to the entropy $S_{\text{mag}}$ was calculated by integrating the $C/T$ versus $T$. The magnetic entropy $S_{\text{mag}}$ at $T_N$ turns out to be 8 J mol$^{-1}$ K$^{-1}$, which is only 46% of $R \ln 8 = 17.3$ J mol$^{-1}$ K$^{-1}$, corresponding to the theoretical value for the Eu$^{2+}$ moments ($S = 7/2$). The reduced value of magnetic entropy at $T_N$ suggests the presence of valence fluctuation/the Kondo effect in this compound. The magnetic entropy reaches the expected theoretical value for divalent Eu moments at around 50 K and it keeps on increasing beyond 50 K. This indicates that the lattice contribution to the heat capacity of EuNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$ is larger than that of LaNi$_2$(P$_{0.5}$Ge$_{0.5}$)$_2$. This, however, does not affect the conclusion that the magnetic entropy at $T_N$ is much less than expected.

3.4. Electrical resistivity

The temperature dependencies of the electrical resistivity $\rho(T)$ of EuNi$_2$(P$_{1-x}$Ge$_x$)$_2$ with $0 \leq x \leq 0.5$ are displayed in Figure 7. For $x \leq 0.4$, the resistivity curves are reminiscent of those observed in heavy fermion Kondo lattice systems, where $\rho(T)$ increases with a decreasing temperature below room temperature, passes through a broad maximum at a temperature related to the Kondo temperature $T_K$ and then decreases at a lower temperature due to the onset of coherence. Such resistivity behavior is typical for heavy fermion Kondo lattice systems [26, 27] containing Ce, Yb or U, but is not so common in Eu-based compounds. For $x = 0.4$, the broad maxima around 100 K become weaker. For a 50% Ge-doped compound, the $\rho(T)$ shows a sudden decrease below $T_N = 12$ K due to Eu-moment ordering, accompanied by a broad resistivity hump at a higher temperature. The loss of resistance below $T_N$ is due to the loss of magnetic scattering in the AFM ordered state. Similar resistivity behavior is observed in many Ce-based magnetically ordered Kondo lattice systems.
3.5. Electronic structure calculations

In order to gain some information on the electronic state of the compounds EuNi$_2$P$_2$ and EuNi$_2$Ge$_2$ (compounds at two extreme ends in the series EuNi$_2$(P$_1$–xGe$_x$)$_2$) we carried out density-functional band-structure calculations using the full potential linear augmented plane-wave plus local orbitals (FP-LAPW + lo) method as implemented in the WIEN2k code [30]. The set of plane-wave expansions K$_\text{MAX}$ was determined as R$_\text{MT} \times$ K$_\text{MAX}$ equal to 7 and the K mesh used was 10 × 10 × 10. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA), as proposed by Pedrew, Burke and Ernzerhof [31]. Additionally, to account for on-site Coulomb interaction, we included a strong Coulomb repulsion in the Eu-4f orbitals at a mean-field level using the GGA + U approximation. For Eu the values of U and J parameters were chosen according to Johannes and Pickett [32]. In addition, the spin–orbit coupling is included in the Eu-4f shell with the second variational method.

The total and partial DOS of EuNi$_2$P$_2$ and EuNi$_2$Ge$_2$ are shown in figure 8. For our GGA + U calculations, we have chosen a value of U = 7.4 eV for effective Coulomb repulsion and a value of J = 0.7 eV for the intra-atomic 4f exchange interaction on the Eu ion, similar to the EuCo$_2$X$_2$ (X = Ge, Si) system [33]. The general shapes of the DOSs are very similar to those of the EuCo$_2$Ge$_2$ or EuCo$_2$Si$_2$ systems [33]. In both compounds, EuNi$_2$P$_2$ and EuNi$_2$Ge$_2$, the deeply lying valence band (below −7.5 eV) is mainly composed of s states of P and Ge atoms and separated by an energy gap of 2.7 eV in EuNi$_2$P$_2$ and of 2.4 eV in EuNi$_2$Ge$_2$ from the main core of valence bands close to the Fermi level (E$_F$). As can be seen from figure 8, the valence bands below the Fermi level are much more extended for EuNi$_2$P$_2$ (0 to −7 eV) as compared to EuNi$_2$Ge$_2$ (0 to −5 eV). The extended DOS is associated with stronger p-d hybridization in EuNi$_2$P$_2$. In both the compounds, the up and down Eu-4f electron spins are polarized and well separated. In the case of EuNi$_2$P$_2$, the bottom of the conduction, i.e. the Eu-4f majority (up) band lies at the Fermi level. The Eu-4f orbitals hybridized slightly with the Ni-3d orbitals yielding the nonintegral valence Eu$^{5+}$ (4f$^{6.5}$) of europium in the EuNi$_2$P$_2$ compound. The calculated DOS is consistent with the photoemission spectroscopy results, where the presence of the Eu-4f density of states at E$_F$ is significant in EuNi$_2$P$_2$ [34]. The magnetic moment comes from the spin-polarized Eu-4f states only (~6.5 µ$_B$). In EuNi$_2$Ge$_2$, the majority of the spin-up channels of the Eu-4f states become fully occupied, as expected. These strongly localized states are placed at about 1 eV below the Fermi level. The 4f states of the minority-spin (dn) channel remain unoccupied and are shifted upwards to 10.5 eV. Evaluating the occupation of the 4f orbital, EuNi$_2$Ge$_2$ is found to be in a magnetic 4f$^7$ state.

4. Conclusions

We have successfully grown single crystals of EuNi$_2$(P$_1$–xGe$_x$)$_2$ with 0 ≤ x ≤ 0.5 using Sn-flux. The evolution from a valence-fluctuating state to a magnetically ordered state in EuNi$_2$(P$_1$–xGe$_x$)$_2$ is presented. A comparative study of the lattice parameters of EuNi$_2$(P$_1$–xGe$_x$)$_2$ suggests that there is an expansion of unit-cell volume across the series from x = 0–1. The expansion of unit-cell volume with an increasing x (Ge) causes the dehybridization of the Eu-4f electron with the conduction electrons, which increases the localized character of the 4f electron. The enhancement of localization results in a decrease in the Eu valence and becomes divalent in the 50% Ge-doped sample. The weakening of the valence fluctuations allows the RKKY exchange to become more effective, leading to a magnetically ordered ground state in EuNi$_2$(P$_0.5$Ge$_0.5$)$_2$. In order to have a clear picture of the valence state of Eu close to the borderline between the magnetic and non-magnetic boundary, it would be worthwhile measuring the photoemission in this system. Furthermore, our results suggest that the antiferromagnetically ordered state of Eu is very stable for x = 1 to x = 0.5, but vanishes abruptly at x = 0.4, which can be considered as a critical concentration ($x_c$) in the EuNi$_2$(P$_1$–xGe$_x$)$_2$ series. In addition, we observed an enhanced Sommerfeld coefficient upon an increasing Ge content. Subsequently, we presented the results of the electronic structure calculations for the two systems EuNi$_2$P$_2$ and EuNi$_2$Ge$_2$, demonstrating the essential dissimilarity of the electronic states close to the Fermi level, which decides the ground state of the Eu ions in the compounds. The electronic structure calculations indicate the strong hybridization and non-integral valence state of Eu in EuNi$_2$P$_2$, whereas Eu-4f states become localized with a divalent character in EuNi$_2$Ge$_2$.

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U B Paramanik et al

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