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Published in:
Journal of Alloys and Compounds

DOI:
[10.1016/0925-8388\(93\)90475-3](https://doi.org/10.1016/0925-8388(93)90475-3)

[Link to publication](#)

Citation for published version (APA):

Bakker, K., Nakotte, H., de Chatel, P. F., Bruck, E. H., de Boer, F. R., Li, J. Y., ... Yang, F. M. (1993). Electronic-Properties of CePdxRh1-xIn. *Journal of Alloys and Compounds*, 200, 79-86. DOI: 10.1016/0925-8388(93)90475-3

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Electronic properties of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$

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(Received April 1, 1993)

Abstract

As part of a systematic research programme on equiatomic ternary compounds of the type RTX (R is a rare earth, T a transition metal and X a metal out of the p block of the periodic table) crystallizing in the ZrNiAl structure, results for $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ ($x=0, 0.2, 0.4, 0.6, 0.8, 0.85, 0.9, 0.95, 1$) are presented. The magnetic properties, specific heat and electrical resistivity as a function of magnetic field and temperature are reported. The development of the electronic properties from CeRhIn with unstable 4f moments towards CePdIn with localized 4f moments is discussed in terms of the influence on the valence state of Ce of the increase in the d-electron concentration due to gradual substitution of Rh in CeRhIn by Pd. The almost trivalent state is found to be most favourable for the formation of the heavy-fermion state.

1. Introduction

Unlike the other rare-earth elements, Ce, Eu and Yb show a variety of valencies in intermetallic compounds depending on for example ion-ion spacing, neighbouring atoms, and lattice pressure. This may be understood in terms of hybridization of the 4f states, lying about 2 eV below the Fermi level, with the conduction-band states, which leads to partial delocalization in the mixed-valence state. In the case of weak hybridization, one of the integer-valence states is stable and can lead to local-moment magnetism. The heavy-fermion state is expected to be in the intermediate region, which means the almost trivalent state in the case of Ce [1].

Compounds of the type CeTIn (T is a late transition metal), which have been studied extensively in recent years [2–16], form in the hexagonal ZrNiAl type structure (Fig. 1), which is an ordered ternary derivative of the Fe_2P structure. In this structure the T atoms occupy the P sites, the Ce atoms the Fe_2 sites and the In atoms the Fe_1 sites [17–20]. The low coordination is indicated by the space group $P6_2m$. The Ce atoms together with one third of the T (transition-metal) atoms form CeT layers, separated by TIn layers, where all In atoms and the remaining T atoms are situated. The shortest Ce–Ce distance is found within the CeT layers (four Ce nearest neighbours) and amounts to 400 pm. There are two second-nearest Ce neighbours

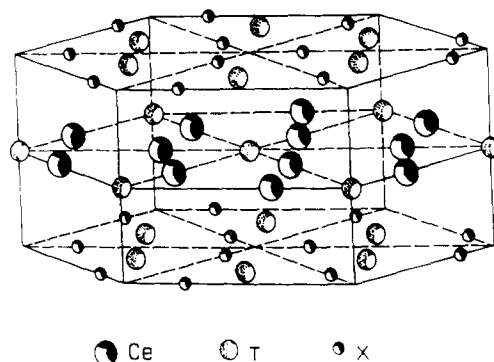


Fig. 1. Schematic representation of CeTX crystallizing in the ZrNiAl type of structure. The volume shown contains three unit cells and nine Ce atoms.

along the c axis separated by a distance equal to the lattice parameter c . It should be noted that the Ce atoms are not arranged centrosymmetrically.

The valency of Ce is governed by f–d hybridization. The compound CeAuIn is of interest because here the d shell of the T component (Au) is filled. It has been shown by Wohleben and Röhler [2], that Ce is almost trivalent (comparable with γ -Ce) in CeAuIn , which indicates that the effect of f–f overlap between neighbouring Ce ions is negligible and f–p hybridization with In is very weak. The stability of the trivalent state of Ce is also reflected in the magnetic ordering at 5.7 K which shows up in the specific heat as an anomaly with an entropy of about $R\ln 2$ [3].

CeRhIn has been identified as a mixed-valence compound [4–7]. This identification was based on lattice parameters, magnetic susceptibility and electrical resistivity data. On the same grounds, CeNiIn also falls in the mixed-valence category [12, 15], albeit with a slightly larger specific heat coefficient ($80 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$, as opposed to $55 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ for CeRhIn). However, CePdIn and CePtIn are clearly heavy-fermion compounds, with C/T values of $0.7 \text{ J K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ and exceeding $1 \text{ J K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ respectively, at 60 mK. CePdIn can be seen as a heavy-fermion system with incipient moment formation: it orders antiferromagnetically at about 1.65 K [8–10]. The magnetic ordering shows up in a maximum in the specific heat and in a distinct change in slope in the electrical resistivity. The entropy connected with the magnetic ordering yields a very low estimated value of $0.4 R \ln 2$ [8]. Other salient features of CePdIn are the occurrence of two maxima in the electrical resistivity at about 3 K and 70 K and a huge, anomalous Hall effect [8]. However, the occurrence of a second maximum in the specific heat at about 0.9 K and an anomalously high electronic specific heat coefficient γ of $700 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ at 70 mK has attracted most attention [11, 12]. It should be noted that extrapolation from temperatures far above T_N yields a γ -value of $123 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$. Furthermore, single-crystal studies reveal strong anisotropy in the magnetic, transport and elastic properties for CePdIn [13, 14].

The primary signature of heavy-fermion behaviour is a strongly enhanced specific heat coefficient, which in various materials is accompanied by the ordering of very small magnetic moments, by superconductivity or by both. To access the relative importance and relevance of these features, it would be useful to characterize the factors determining the degree of f-electron delocalization. If this were possible, one would expect the strongest mass enhancement at the borderline of localization. In this context, series of quasiternary compounds, bridging the gap between mixed-valence and magnetically ordered heavy-fermion ternary compounds are of paramount interest. Fujita *et al.* [15] studied CePd_{1-x}Pt_xIn with this in mind. Here we present some measurements of the pseudo-ternary system CePd_xRh_{1-x}In. As Pd and Rh have almost the same atomic volume, this series is ideally suited for the study of the influence of electronic properties, hybridization in particular, on the f-electron states.

2. Experimental details

The parent compounds CeRhIn and CePdIn were prepared as polycrystalline materials by arc-melting appropriate amounts of the constituents, with a minimum purity of 99.9% in the case of Ce and 99.99%

for the other elements, under a Ti-gettered argon atmosphere. In order to account for evaporation losses of In during the melting, about 2 wt.% In was added. The polycrystalline pseudo-ternaries of CePd_xRh_{1-x}In with x equal to 0.2, 0.4, 0.6, 0.8, 0.85, 0.9 and 0.95 were prepared by arc-melting appropriate quantities of bulk materials taken from the parent compounds under a Ti-gettered argon atmosphere. Additional heat treatment was applied in order to homogenize the samples. To this end, these compounds were wrapped in tantalum foil, sealed in separate quartz tubes under 300 mbar argon atmosphere and annealed for 10 days at 800 °C.

The temperature dependence of the magnetic susceptibility was measured in the temperature interval 1.8–300 K by a pendulum magnetometer. In order to minimize the effect of possible preferential orientation present in the bulk materials these measurements were taken on fixed powders. To this end, the bulk samples were ground by a tungsten carbide ball until powder with a typical grain size smaller than 100 μm was obtained. On the basis of experience with related compounds [21] it can be expected that the particles of such a fine powder are almost all single crystalline. This powder in turn was fixed in random orientation by glue, which simulates an “ideal” polycrystal.

The magnetization was measured at 4.2 K in semi-continuous fields up to 35 T in the Amsterdam High-Field Installation. These measurements were taken on two kinds of sample: powder in random orientations fixed in frozen alcohol (fixed powder) and powder free to be oriented by the applied field (free powder). While a fixed powder again is thought to represent an “ideal” polycrystal, the result obtained for free powder is representative of magnetization along the easy magnetization direction.

The temperature dependence of the specific heat was measured on bulk pieces between 1.2 and 40 K using a standard adiabatic method. For $x \geq 0.6$ specific heat measurements were extended down to 320 mK using a standard relaxation–time method.

Between 4.2 and 300 K, the temperature dependence of the electrical resistivity was measured on bulk rods, which were cut by spark erosion from the buttons, using a standard four-point a.c. technique. For Pd concentrations $x \geq 0.6$ these measurements were extended down to 300 mK.

3. Results and discussion

The quality of the CePd_xRh_{1-x}In samples was checked by microprobe analysis, which revealed the proper composition and the absence of impurity phases except for a small amount of cerium oxide in some samples,

which was most probably introduced in the form of oxides present in the Ce starting material and/or further oxidation of the samples with time. The specific heat of such samples was almost unaffected by the presence of oxides, except for a small anomaly close to 6 K where Ce_2O_3 orders antiferromagnetically [22]. From the entropy connected with this anomaly, the oxide content could be estimated to be less than 2%, in good agreement with the results from microprobe analysis.

The lattice parameters of the parent compounds determined by X-ray diffraction were found to be in good agreement with the literature values [4, 19]. The variation of the lattice parameters and unit cell volume with composition is presented in Fig. 2. The effect of substitution of Rh by Pd on the lattice parameter is the largest in the basal plane. The a parameter increases almost linearly with Pd concentration, the total increase being about 2% which exceeds the total relative change in the c parameter by a factor of four. The change in the latter parameter is not monotonic, the initial increase is followed by a partial decrease for $x \geq 0.8$. Nevertheless, the unit cell volume increases monotonically with increasing Pd concentration x .

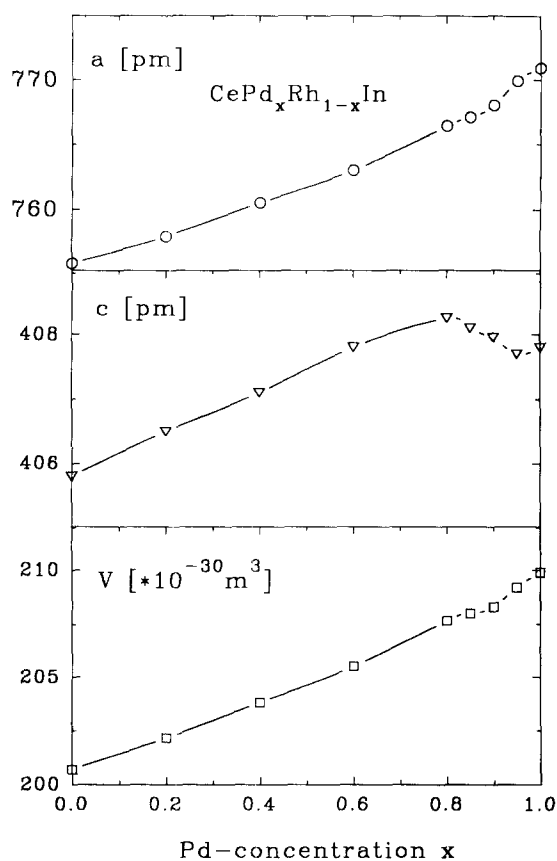


Fig. 2. Dependence on concentration of the lattice parameters a and c and of the unit cell volume of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$. The lines are guides to the eye.

3.1. Magnetic properties

The temperature dependence of the magnetic susceptibility of the $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ compounds is displayed in Fig. 3. For the samples with lower Pd content ($x < 0.4$) a maximum in the magnetic susceptibility, which is typical of mixed-valence behaviour, is observed. For CeRhIn and $\text{CePd}_{0.2}\text{Rh}_{0.8}\text{In}$ these maxima are seen around 150 and 80 K respectively. At low temperatures, a steep increase in the magnetic susceptibility is observed, which we attribute to the presence of Ce^{3+} ions stabilized by lattice defects or impurities of other rare-earth ions. Combining the measurements of magnetic susceptibility and high-field magnetization (Figs. 5 and 6), we can estimate the amount of Ce^{3+} impurities necessary for the low-temperature upturn in the magnetic susceptibility. Therefore, the intrinsic magnetic susceptibility at 4.2 K was determined from the high-field magnetization results in fields in which Ce^{3+} moments are thought to be saturated. Taking the obtained values for the intrinsic magnetic susceptibility and comparing these with the measured values we calculate the amount of Ce^{3+} impurities, assuming that the additional contribution of these impurities follows a Curie law. The influence of the impurities was found to be most prominent in the Rh-rich samples, yielding values of about 2% Ce^{3+} impurities, while for $x > 0.4$ the effect of less than 1% impurity was detected.

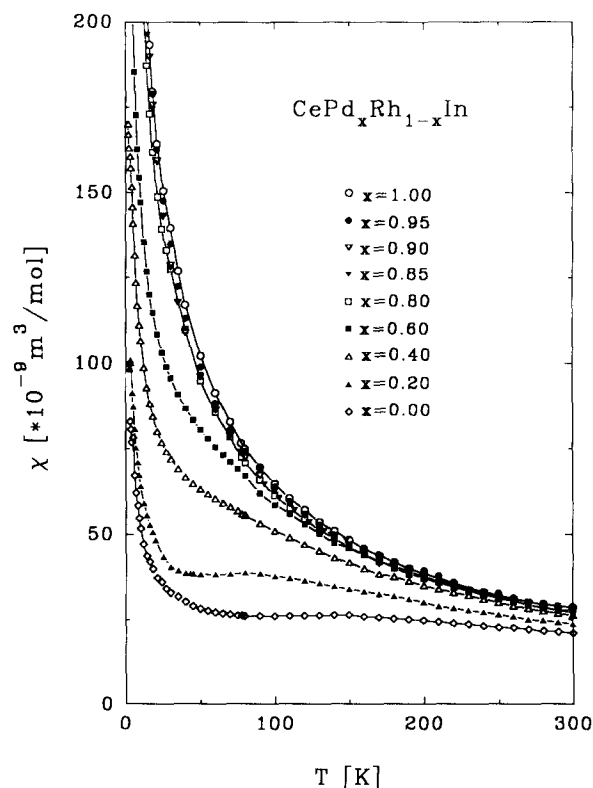


Fig. 3. Dependence on temperature of the magnetic susceptibility of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$. The lines are guides to the eye.

Subtracting such a Curie term yields a maximum for $\text{CePd}_{0.4}\text{Rh}_{0.6}\text{In}$, while no maximum was found for $\text{CePd}_{0.6}\text{Rh}_{0.4}\text{In}$. For $x \geq 0.8$ the temperature dependence of the magnetic susceptibility hardly depends on the composition. In Fig. 4, the temperature dependence of the inverse susceptibility is presented for some samples. For $x \geq 0.6$, the compounds are seen to obey a Curie–Weiss law above about 50 K. While in these compounds the effective moment μ_{eff} is independent of x within experimental error and close to the free-ion value of for Ce^{3+} ($2.54\mu_{\text{B}}$), a successive reduction in the paramagnetic Curie temperatures θ_{p} with increasing Rh content from -48 K for CePdIn to -69 K for $\text{CePd}_{0.6}\text{Rh}_{0.4}\text{In}$ is found (Table 1).

The magnetic isotherms obtained on free powders at 4.2 K in applied magnetic fields up to 35 T are shown in Fig. 5. As mentioned above, the samples of the $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ series contain some impurities, which affect the initial slope of the magnetization curves. Unlike in the case of magnetic susceptibility, the effect of impurities is strongest in the Pd-rich samples. Assuming the “impurities” to be oxide precipitates, we can speculate this discrepancy to be due to deterioration of the samples, since the high-field measurements were taken first after preparation of the samples whereas the magnetic susceptibility was measured much later

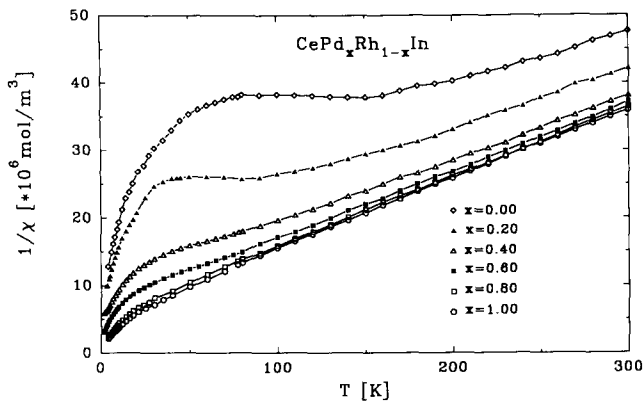


Fig. 4. Dependence on temperature of the inverse magnetic susceptibility of some $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ compounds. The lines are guides to the eye.

TABLE 1. Curie–Weiss fitting parameters for $\text{CePd}_x\text{Rh}_{1-x}\text{In}$.

Pd content x	Effective moment μ_{eff} (μ_{B} per Ce atom)	Paramagnetic Curie temperature θ_{p} (K)
1.00	2.49	-48
0.95	2.52	-52
0.90	2.47	-51
0.85	2.49	-57
0.80	2.51	-60
0.60	2.54	-69

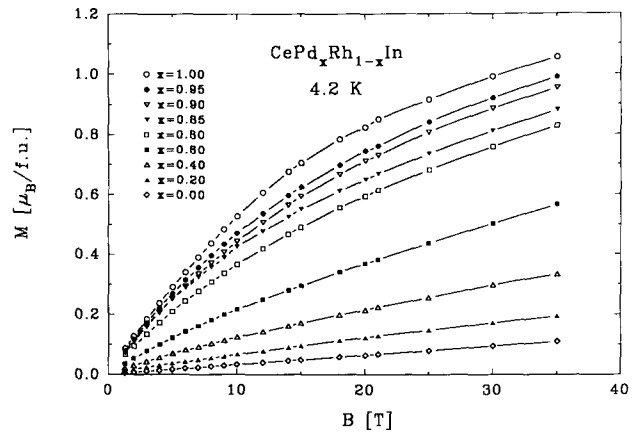


Fig. 5. Dependence on field of the magnetization of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ measured on powder free to be oriented in the applied field.

and further oxidation of the samples with time cannot be excluded. Support for the validity of this assumption is found in the fact that the small magnetization (less than $0.02\mu_{\text{B}}$ per f.u.) at 0 T determined by extrapolation from the linear part of the magnetization curves in low fields is consistent with an oxide content below 1%, which in all cases is smaller than the values obtained from the magnetic susceptibility results. Therefore we can attribute this easily saturated magnetization to Ce^{3+} in Ce_2O_3 and other “impurities”.

The magnetization of free powders at 35 T increases almost linearly with x for $x \geq 0.4$, yielding a value of $1.07\mu_{\text{B}}$ per f.u. for CePdIn . Although some tendency towards saturation is observed for $x \geq 0.6$, a considerable differential susceptibility remains even in the highest field applied. The magnetic response is the lowest and almost linear for CeRhIn , yielding a value of about $0.11\mu_{\text{B}}$ per f.u. in 35 T. Almost straight magnetization curves are also found for $\text{CePd}_{0.2}\text{Rh}_{0.8}\text{In}$ and $\text{CePd}_{0.4}\text{Rh}_{0.6}\text{In}$ with magnetization values at 35 T, which exceed by a factor of 1.8 and 3 respectively that of CeRhIn .

A considerable difference in the magnetization values of free and fixed powders is seen for $x > 0.6$ (Fig. 6). At 35 T, the ratio $M_{\text{fix}}/M_{\text{free}}$, which can be taken as a measure of the anisotropy, is 0.84 for CePdIn . Such a value is indicative of a basal-plane type of anisotropy [21]. With increasing Rh content, $M_{\text{fix}}/M_{\text{free}}$ decreases approximately linearly and for $\text{CePd}_{0.6}\text{Rh}_{0.4}\text{In}$ no indication of anisotropy is found. This behaviour indicates the strong dependence of the anisotropy on the surrounding transition element. Pd neighbours seem to cause preferential orientation of the spins, while Rh neighbours do not. However, the observed development of anisotropy may be an artefact of the powder-sample technique. The rather low magnetic moments of the Rh-rich compounds may not be sufficient to orient the

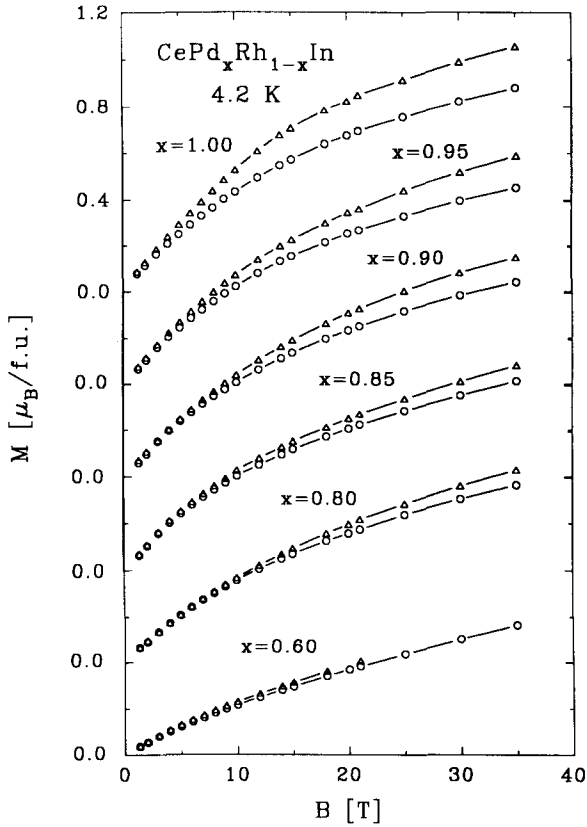


Fig. 6. Development of anisotropy in the field dependence of the magnetization with increasing Pd content in $\text{CePd}_x\text{Rh}_{1-x}\text{In}$. The triangles represent measurements on powder free to be oriented in the field, whereas the circles represent results obtained on powder fixed in random orientation by frozen alcohol.

particles, in which case the free-powder and fixed-powder results would be indistinguishable.

3.2. Specific heat

The high temperature part of the specific heat displayed in Fig. 7 is dominated by the phonon contribution with Debye temperatures slightly below 200 K and is hardly affected by Pd substitution. From the similarity in atomic masses of Pd and Rh a similar phonon spectrum may be expected. At low temperatures, drastic changes are observed with increasing Pd content, connected with both a change in the electronic contribution and the occurrence of long-range magnetic order. Up to 30 K, the C_p/T vs. T^2 plot for CeRhIn is perfectly linear. The electronic contribution γ of about $40 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ is consistent with the mixed-valence state. Compared with CeRhIn , γ is considerably enhanced for $\text{CePd}_{0.2}\text{Rh}_{0.8}\text{In}$ and yields $78 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$. For $x=0.4$ and $x=0.6$, pronounced upturns are observed in C_p/T at low temperatures, yielding extrapolated values of about 280 and $700 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ at zero temperature respectively. Usually, such upturns are fitted with an additional $T^3 \ln T$ term resulting from para-

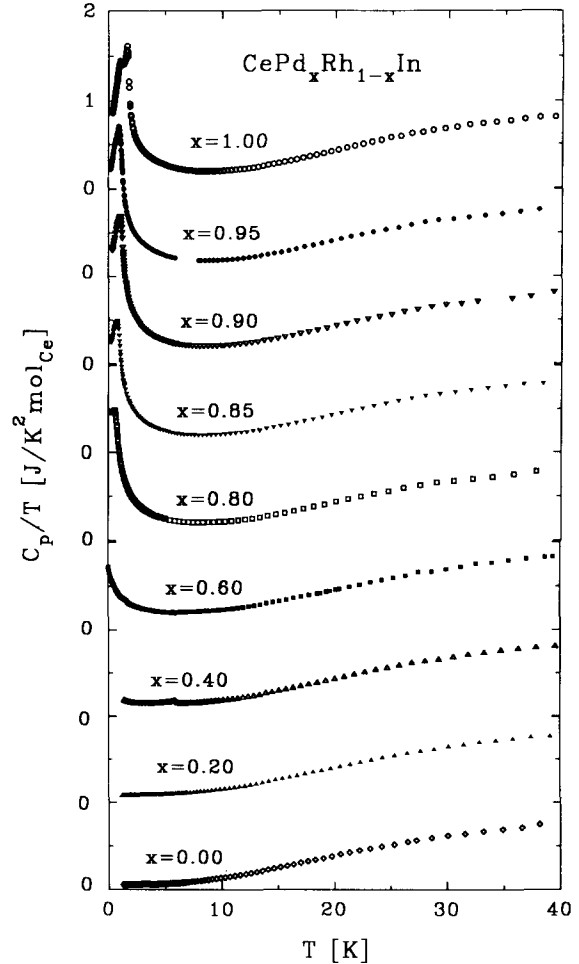


Fig. 7. Dependence on temperature of the specific heat of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ in the representation C_p/T vs. T .

magnon theory [23]. However, this additional term fits the data for $x=0.4$ and 0.6 only in a very restricted temperature range, which indicates a different origin of the upturns in the compounds under investigation. For higher Pd concentrations magnetic order appears. Owing to the low transition temperatures the electronic contribution to the specific heat cannot be reliably estimated for $x \geq 0.8$. By extrapolation of the linear part in the C_p/T vs. T^2 plot found at temperatures above T_N , we obtain slightly higher values than $120 \text{ mJ K}^{-2} \text{ mol}_{\text{Ce}}^{-1}$ for $x \geq 0.8$. To study the development of the magnetic ordering in more detail, the measurements were extended down to 320 mK for $x \geq 0.6$ (Fig. 8). No anomaly, which could be connected with magnetic order, was found for $\text{CePd}_{0.6}\text{Rh}_{0.4}\text{In}$. For $\text{CePd}_{0.8}\text{Rh}_{0.2}\text{In}$ a maximum is detected at about 0.65 K, which is shifted to about 0.9 and 1 K for $\text{CePd}_{0.85}\text{Rh}_{0.15}\text{In}$ and $\text{CePd}_{0.9}\text{Rh}_{0.1}\text{In}$ respectively. With a further increase in the Pd content, this peak shows up at approximately the same temperature for $\text{CePd}_{0.95}\text{Rh}_{0.05}\text{In}$. Finally, two distinct maxima are found in CePdIn at temperatures of about 1 K and 1.7 K. The latter temperature has

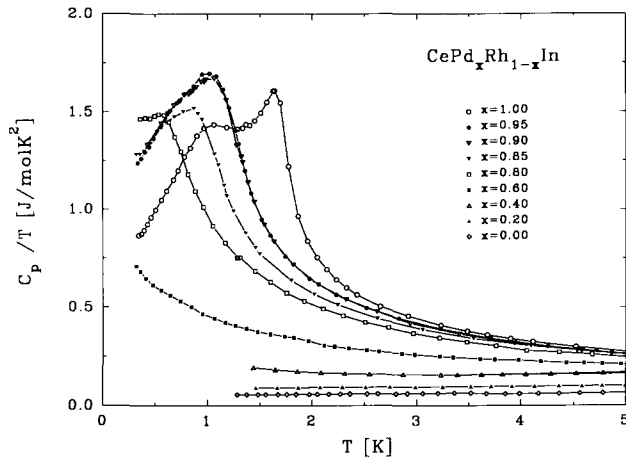


Fig. 8. Low-temperature part of the temperature dependence of the specific heat of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ for $x \geq 0.6$ in the representation C_p/T vs. T . The lines are guides to the eye.

been identified as the temperature of antiferromagnetic ordering [8], whereas the peak at 1 K is not yet understood. Unfortunately, on the basis of experiments of the present series, we cannot conclude whether and in which way the low-temperature anomaly of CePdIn is affected by the substitution as the maxima for $x \geq 0.8$ may consist of contributions of both peaks. The entropy connected with the magnetic ordering is about $0.4 R \ln 2$ for CePdIn and is further reduced with increasing Rh concentration, which may be related to a partial delocalization.

3.3. Electrical resistivity

The temperature dependence of the electrical resistivity of the $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ compounds is summarized in Fig. 9. At about 3 K and 70 K, the resistivity of CePdIn exhibits two maxima, which is characteristic of many heavy-fermion and Kondo-lattice systems [24]. The drop below the low-temperature maxima can be related to the onset of coherence in the Kondo lattice. The double-peak structure is indicative of an interplay of Kondo scattering and crystal-field effects. For $x \geq 0.85$, both maxima are seen to shift towards lower temperatures with increasing Rh content. For $\text{CePd}_{0.8}\text{Rh}_{0.2}\text{In}$, only the low-temperature maximum remains. For $\text{CePd}_{0.6}\text{Rh}_{0.4}\text{In}$ this second maximum also vanishes, but a steep increase at low temperatures reflects the importance of spin fluctuations in this compound. For higher Rh content, the electrical resistivity becomes a monotonically increasing function of temperature, showing quadratic temperature dependence at low temperatures.

The occurrence of magnetic ordering for $x \geq 0.8$ is manifested by different slopes in the electrical resistivity below and above the ordering temperature. From the low-temperature part of the electrical resistivity (Fig. 10) ordering temperatures are found at 1.8, 1.3, 1.3,

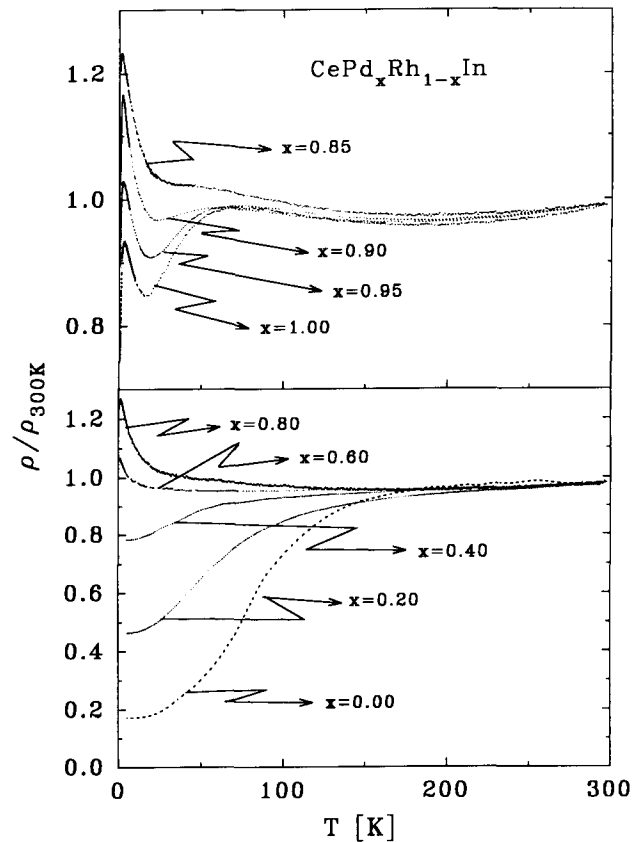


Fig. 9. Dependence on temperature of the electrical resistivity of $\text{CePd}_x\text{Rh}_{1-x}\text{In}$ normalized to the room temperature value. The result for pure CeRhIn (dashed curve) is taken from ref. 5.

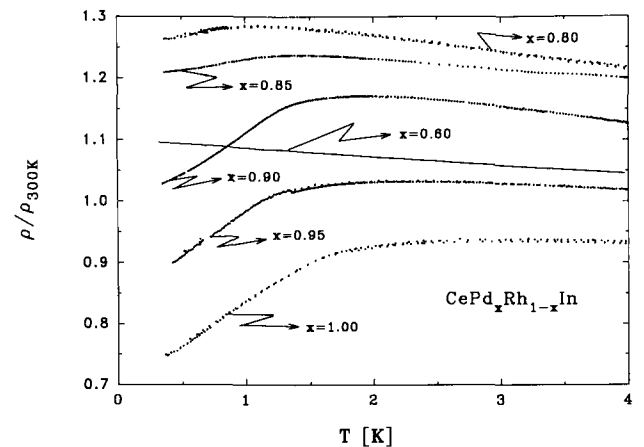


Fig. 10. Low temperature part of the dependence on temperature of the electrical resistivity of $\text{CePd}_x\text{Rh}_{1-x}$ for $x \geq 0.6$ normalized to the room temperature value.

1.1 and 0.8 K for x equal to 1, 0.95, 0.9, 0.85 and 0.8 respectively. These values are about 0.2–0.3 K higher than the ordering temperatures obtained from the maxima in the specific heat, which may be due to the occurrence of fluctuations close to the ordering temperature. The second maximum in CePdIn , at about 1 K, shows up as an inflection point in the electrical

resistivity at nearly the same temperature. A maximum in the derivative is also observed for the other samples which exhibit magnetic order. The temperature of this maximum does not change for $x \geq 0.85$ and decreases to about 0.7 K for CePd_{0.8}Rh_{0.2}In. This may indicate that both anomalies seen in CePdIn are present in the compounds with $x \geq 0.8$, though invisible in our specific heat measurements where the maxima contain contributions of both peaks. However, as these measurements were taken on polycrystalline samples, where certain effects could be introduced by preferential orientation of the grains, such a conclusion has to be drawn with caution.

4. Conclusions

Our comprehensive set of measurements on nine different quasiternary CePd_xRh_{1-x}In alloys indicates a gradual emergence of the heavy-fermion state in this series. The results do not suggest a sharp distinction between the mixed-valence and heavy-fermion states. As anticipated, the mass enhancement, reflected in the specific heat coefficient γ , increases with increasing Pd content and reaches a maximum before magnetic ordering sets in at $x=0.8$. CePd_{0.6}Rh_{0.4}In is a heavy-fermion system showing no sign of magnetic ordering above 300 mK. The concentration range $0.6 < x < 0.8$ remains of interest, although inhomogeneities and preferential site occupation may hamper the fine tuning of materials in this narrow range.

Unlike in CeNi_xPt_{1-x}Si [25], where a distinct change in slope in the unit cell volume *vs.* composition diagram indicates the onset of mixed valency, in CePd_xRh_{1-x}In we find no such feature. The non-monotonic dependence on composition of the lattice parameter c has little effect on the volume, which remains a monotonic function of x throughout the entire concentration range. When using the unit cell volume *vs.* composition as an indicator of Ce valency, one should bear in mind that there is an unexplained irregularity in the volume of RTIn compounds. As pointed out by Rossi *et al.* [17], the unit cell volume of such compounds scales reasonably with the atomic volume of the T component, with the exception of the Pd compounds which deviate from the scaling behaviour towards larger volumes. As the occupancy of the 4d shell of Pd is a factor influencing the unit cell volume, under these circumstances the latter may not be a good measure of the Ce valency.

With respect to CeAuIn, the reduction of the magnetic ordering temperature and the low entropy of this transition in CePdIn must be attributed to a weak delocalization of the Ce 4f states, due to hybridization with Pd 4d states. The enhancement of the electronic contribution to the specific heat, the temperature depen-

dence of the electrical resistivity and the high-field magnetic moment are comparable with CeAl₂, which also orders magnetically [26]. Therefore, similar values for the characteristic temperature and the valency, which amount to about 10 K and 3 for CeAl₂ respectively, can be expected for CePdIn. This is also reflected in the temperature dependence of the electrical resistivity and the high Hall coefficient at low temperatures [8]. The high γ value of the specific heat corresponds to an enhanced density of states in the region where about half of the Pd atoms are replaced by Rh, which can be considered to reflect an increase in the “chemical” pressure on CePdIn by more than 20 kbar [16]. With increasing Pd content in the mixed-valence system CeRhIn, a reduction in the characteristic temperature amounting to about 150 K, which is deduced from the maximum in the temperature dependence of the magnetic susceptibility, is observed. For $x \leq 0.6$, the substitution of Rh by Pd leads to the destruction of the mixed-valence state. In consequence, Ce in CePd_{0.6}Rh_{0.4}In is almost trivalent, but RKKY types of interactions are not yet sufficiently strong. The properties of this compound resemble those of CePtIn [27].

Our measurements do not give direct information on the mechanism of f electron delocalization in these compounds. However, a plausible explanation of the results is given in terms of hybridization with 4d states [28]. Indeed, such hybridization should not affect the 4f states in CeAuIn and should have an increasingly important delocalizing effect as the 4d shell is depopulated in going from CePdIn to CeRhIn. Although, the mechanism is easiest to visualize in terms of overlap between neighbouring atoms, it is by no means meant to imply isolated covalent bonds. Undoubtedly, the 4d states of Pd and Rh form a common band and it is the gradual change in the nature and the occupancy of this band that leads to further delocalization as the Rh content is increased. The smooth concentration dependence and the absence of local environment effects can only be understood if hybridization with extended Bloch-like states is involved.

Acknowledgments

This work was supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). Part of the work of one of us (Yang Fuming) was supported by the National Science Foundation of China. This work has partly been carried out within the scientific exchange programme between China and The Netherlands.

References

- 1 N.B. Brandt and V.V. Moshchalkov, *Adv. Phys.*, **33** (1984) 373.
- 2 D. Wohlleben and J. Röhrler, *J. Appl. Phys.*, **55** (1984) 1904.
- 3 H.R. Pleger, E. Brück, E. Braun, F. Oster, A. Freimuth, B. Pollit, B. Roden and D. Wohlleben, *J. Magn. Magn. Mater.*, **63-64** (1987) 107.
- 4 S.K. Malik, D.T. Adroja, B.D. Padalia and R. Vijayaraghavan, *Physica B*, **163** (1990) 89.
- 5 M.N. Nyayate, S.H. Devare, S.K. Malik, D.T. Adroja and H.G. Devare, *Phys. Lett. A*, **151** (1990) 547.
- 6 D.T. Adroja, S.K. Malik, B.D. Padalia and R. Vijayaraghavan, *Phys. Rev. B*, **39** (1989) 4831.
- 7 D.T. Adroja and S.K. Malik, *J. Magn. Magn. Mater.*, **100** (1991) 126.
- 8 E. Brück, M. van Sprang, J.C.P. Klaasse and F.R. de Boer, *J. Appl. Phys.*, **63** (1988) 3417.
- 9 H. Fujii, Y. Uwatoko, M. Akamaya, K. Satoh, Y. Maeno, T. Fujita, J. Sakurai, H. Kamimura and T. Okamoto, *Jpn. J. Appl. Phys.*, **26** (1987) 549.
- 10 Y. Maeno, M. Takahashi, T. Fujita, Y. Uwatoko, H. Fujii and T. Okamoto, *Jpn. J. Appl. Phys.*, **26** (suppl. 26-3) (1987) 545.
- 11 K. Satoh, Y. Maeno, T. Fujita, Y. Uwatoko and H. Fujii, *J. Phys. Coll. (Paris)*, **49** (1988) C8-779.
- 12 K. Satoh, T. Fujita, Y. Maeno, Y. Uwatoko and H. Fujii, *J. Phys. Soc. Jpn.*, **59**(2) (1990) 692.
- 13 T. Suzuki, M. Nohara, T. Fujita, T. Takabatake and H. Fujii, *Physica B*, **165-166** (1990) 421.
- 14 H. Fujii, M. Nagasawa, H. Kawanaka, T. Inoue and T. Takabatake, *Physica B*, **165-166** (1990) 435.
- 15 T. Fujita, T. Suzuki, S. Nishigori, T. Takabatake, H. Fujii and J. Sakurai, *J. Magn. Magn. Mater.*, **108** (1992) 35.
- 16 M. Kurisu, T. Takabatake and H. Fujii, *J. Magn. Magn. Mater.*, **90-91** (1990) 469.
- 17 D. Rossi, R. Ferro, V. Contardi and R. Marazza, *Z. Metallkd.*, **68** (1977) 493.
- 18 S. Cirafici, A. Palenzona and F. Canepa, *J. Less-Common Met.*, **107** (1985) 179.
- 19 R. Ferro, R. Marazza and G. Rambaldi, *Z. Metallkd.*, **65** (1974) 37.
- 20 D. Rossi, D. Mazzone, R. Marazza and R. Ferro, *Z. Anorg. Allg. Chem.*, **507** (1983) 235.
- 21 V. Sechovsky and L. Havela, in E.P. Wohlfarth and K.H.J. Buschow (eds.), *Ferromagnetic Materials*, Vol. 4, North-Holland, Amsterdam, 1988, p. 309.
- 22 M.J. Besnus, J.P. Kappler and A. Meyer, *J. Phys. F*, **13** (1983) 597.
- 23 S. Doniach and S. Engelsberg, *Phys. Rev. Lett.*, **17** (1966) 750.
- 24 S. Horn, M.A. Edwards, J.D. Thompson and R.D. Parks, *J. Magn. Magn. Mater.*, **52** (1985) 385.
- 25 W.H. Lee, H.C. Ku and R.N. Shelton, *Phys. Rev. B*, **36** (1987) 5739.
- 26 J. Aarts, F.R. de Boer, S. Horn, F. Steglich and D. Meschede in L.M. Falicov, W. Hanke and M.B. Maple (eds.), *Valence Fluctuations in Solids*, North-Holland, Amsterdam, 1981, p. 301.
- 27 J. Aarts, F.R. de Boer, S. Horn and F. Steglich, *Physica B*, **107** (1981) 381.
- 28 T. Fujita, K. Satoh, Y. Maeno, Y. Uwatoko and H. Fujii, *J. Magn. Magn. Mater.*, **76-77** (1988) 133.
- 29 D.D. Koelling, B.D. Dunlap and G.W. Crabtree, *Phys. Rev. B*, **31** (1985) 4966.